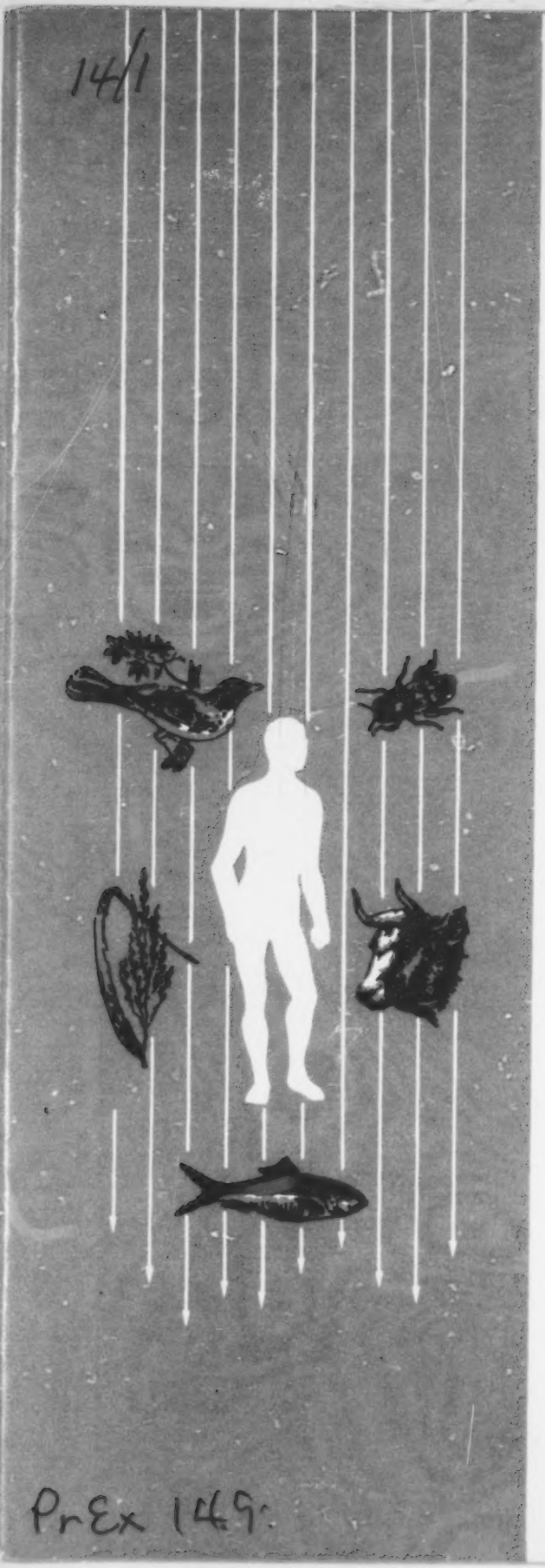

PESTICIDES MONITORING JOURNAL

JUNE 1980

VOLUME 14 NUMBER 1

PEMJAA (14) 1-34 (1980)

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The Monitoring Panel consists of representatives of the Agricultural Research Service, Animal and Plant Health Inspection Service, Extension Service, Forest Service, Department of Defense, Fish and Wildlife Service, Geological Survey, Food and Drug Administration, Environmental Protection Agency, National Marine Fisheries Service, National Science Foundation, and Tennessee Valley Authority.

The *Pesticides Monitoring Journal* is published by the Chemical Information Division, Office for Program Integration and Information, Office of Pesticides and Toxic Substances, U.S. Environmental Protection Agency.

Pesticide monitoring activities of the Federal Government, particularly in those agencies represented on the Monitoring Panel which participate in operation of the national pesticides monitoring network, are expected to be the principal sources of data and articles. However, pertinent data in summarized form, together with discussions, are invited from both Federal and non-Federal sources, including those associated with State and community monitoring programs, universities, hospitals, and nongovernmental research institutions, both domestic and foreign. Results of studies in which monitoring data play a major or minor role or serve as support for research investigation also are welcome; however, the Journal is not intended as a primary medium for the publication of basic research. Publication of scientific data, general information, trade names, and commercial sources in the *Pesticides Monitoring Journal* does not represent endorsement by any Federal agency.

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HUMANS

Organochlorine Contaminants in Human Milk from Slavonia Province, Yugoslavia, 1978

M. Kodric-Smit,[1] Zdenko Smit,[2] and K. Olie [3]

ABSTRACT

Organochlorine residues were determined in human milk samples from an agricultural area of Slavonia, Yugoslavia. Concentrations of pentachlorobenzene, hexachlorobenzene, α-, β-, γ-isomers of benzene hexachloride, heptachlor, aldrin, DDE, TDE, and DDT were determined by gas chromotography (GC). Confirmation was carried out by computerized GC–mass spectrometry. The most abundant contaminant was p,p'-DDE (range, 42.0–418.5 μg/kg (ppb)).

Introduction

For many years, organochlorine pesticides have been investigated because of their toxicity and persistence. Although human milk is the best natural food for babies, it can become a primary depository for organochlorine contaminants. Numerous authors worldwide have reported relatively high levels of these contaminants in human milk (*1, 3–7, 11*).

The present work examines the levels of organchlorine contaminants in the human milk samples from Slavonia Province, Yugoslavia.

Sampling and Analysis

Ten human milk samples were collected at Children's Hospital of Osijek during the first half of 1978. Volunteer donors were lactating mothers, 17 to 41 years old. Samples were manually expressed at one to four months postpartum into precleaned glass bottles. The samples were stored at −30°C until analysis.

Each 10-g milk sample was extracted twice by shaking it for 15 minutes with a mixture of 15 ml acetone and 20 ml hexane. The extract was centrifuged. The hexane layer was collected by pipetting and was concentrated under a stream of nitrogen; the lipids were redissolved in hexane. Cleanup was performed with concentrated H_2SO_4 according to the procedure of Veierov and Aharonson (*10*). Cleaned extracts were analyzed by electron-capture gas chromatography (GC) for the following organochlorine contaminants: pentachlorobenzene, hexachlorobenzene (HCB), α-, β-, and γ-isomers of benzene hexachloride (BHC), heptachlor, aldrin, DDE, TDE, and DDT. Instrument parameters and operating conditions were as follows:

Chromatograph:	Varian Series 1400
Detector:	Sc-H^3 electron capture
Column:	glass, capillary, 0.3 mm × 27 meters, coated with OV-101 after HCl treatment
Split ratio:	1:25
Chromatograph:	Tracor 550
Detector:	Ni^{63} electron capture
Column:	glass, 2 mm × 2 meters, packed with 3 percent SE-30 on 80–100-mesh Chromosorb W-AW

Confirmation was carried out by computerized GC–mass spectrometry (MS) with the following instrument parameters and operating conditions:

GC–MS-Computer System:	Hewlett-Packard 5710A GC and Hewlett-Packard 5980A MS interfaced with Hewlett-Packard 5933A Data System	
Column:	glass, 2 mm × 2 meters, packed with 0.2 percent Carbowax 20M on 100–120-mesh Chromosorb W-AW	
Temperatures, °C:	jet separator	350
	ion source	180
	analyzer	110
Electron energy:	70 eV	
Scan rate:	80 amu/second	

In addition to the usual computer program for GC–MS, the authors used a special program called the halo-test (*8*) for searching organochlorine compounds from stored GC–MS data. The search was performed after each GC–MS run.

Results and Discussion

All samples analyzed contained some of the following organochlorine contaminants: pentachlorobenzene, hexachlorobenzene, α- and β-isomers of BHC, *p,p'*-DDE, *p,p'*-TDE, and *p,p'*-DDT. Results of quantitative deter-

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TABLE 1. *Concentrations of organochlorine contaminants in human milk samples from Slavonia Province, Yugoslavia—1978*

Compound	Sample size, n	Residues, μg/kg	
		Range	Av. Concn
Pentachlorobenzene	6	0–3.4	2.0
Hexachlorobenzene	10	1.6–17.1	5.9
α-BHC	5	<0.1	—
β-BHC	10	4.1–18.6	9.1
p,p'-DDE	10	42.0–418.5	175.7
p,p'-TDE	5	<1	—
p,p'-DDT	10	8.0–135.4	50.8

NOTE: Results are not corrected for recovery. Investigated recovery for the procedure in general was 90–98 percent.

minations of pentachlorobenzene, HCB, β-BHC, *p,p'*-DDE, and *p,p'*-DDT are shown in Table 1.

p,p'-DDE was found most frequently and in the highest concentrations (42.0–418.5 μg/kg).

The best separation of BHC isomers and hexachlorobenzene (HCB) was obtained on the column packed with 0.2 percent Carbowax 20M prepared according to Aue et al. (*2*) which separates isomers of other organochlorine compounds (*9*). Levels of β-BHC, HCB, and pentachlorobenzene were significantly lower than *p,p'*-DDE levels but still high in comparison to levels of α-BHC which was found in traces only. γ-BHC was not found in measurable amounts (detection limit 1 pg), although the most used foodstuffs investigated in our laboratory (unpublished data) and in other laboratories (*12*) contained large amounts of it.

Acknowledgment

The authors thank O. Hutzinger for interest and helpful suggestions, and Dr. Mandic for collecting the milk samples.

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FOOD AND FEED

Residue Dynamics of Acephate and Methamidophos in Urban Dooryard Citrus Foliage, Pompano Beach, Florida—August–September 1978 [1]

George E. Fitzpatrick [2] and Michael D. Bogan [2]

ABSTRACT

Residues of acephate and its toxic metabolite methamidophos, attributable to the State-Federal program for eradication of the citrus blackfly (CBF) [Aleurocanthus woglumi *Ashby*] *on citrus foliage, were assessed in urban areas in Pompano Beach, Florida. Eighteen dooryard citrus trees were sampled on two line transects, each ca 1.6 km long, along two city streets. The trees were sampled twice monthly for five months, beginning before chemical treatments were applied, continuing through the acephate treatment period, and ending when residues decreased below the limits of detection. Acephate and methamidophos residues, as high as 302.5 ppm and 15.8 ppm, respectively, were detected on leaves within one day after the first of a series of three treatments. Significant conversion of acephate to methamidophose was observed. Of the 143 samples collected, 114 contained measurable residues of both compounds; methamidophos accounted for an average of 19 percent of the total residues. Both compounds degraded rapidly, however, and residues averaged below 1 ppm approximately four weeks after the third treatment in the series. Average foliar half-lives for acephate and methamidophos were 8.93 days (SD = 2.52) and 8.40 days (SD = 2.55), respectively.*

Introduction

The citrus blackfly (CBF), *Aleurocantus woglumi* Ashby, was the target of an eradication program conducted jointly by the Florida Department of Agriculture and Consumer Services, Division of Plant Industry (DPI), and the U.S. Department of Agriculture, Animal and Plant Health Inspection Service (APHIS), in southern Florida during 1976–1979. An aleyrodid insect of Asian origin, *A. woglumi* were found as dooryard citrus infestations in the Fort Lauderdale area in early 1976. Other infestations were subsequently discovered throughout Broward County and in Brevard, Dade, Palm Beach, Collier, Martin, Okeechobee, Indian River, and St. Lucie Counties, as well.

Although a number of insecticides had been shown to be effective against *A. woglumi* (*2, 3, 7, 8, 11*), acephate was selected for the eradication program because of acceptable efficacy (*7*), very low acute mammalian toxicity (*5*), and its availability in a soluble powder formulation that would reduce real or potential phytotoxic damage to host plants and other adjacent ornamental plants prevalent in urban areas. Moreover, acephate was shown to have relatively low acute negative impact on biological control agents of *A. woglumi* (*1*).

Although acephate was not registered for CBF control, a crisis exemption was granted by the U.S. Environmental Protection Agency (EPA), allowing its application for citrus blackfly eradication. Acephate was to be applied to all citrus plants as well as mango (*Mangifera indica*) and Surinam-cherry (*Eugenia uniflora*) in Palm Beach, Broward, and Dade Counties. In other Florida counties, only the areas infested were sprayed. It was diluted to 0.6 g/liter and applied with hydraulic sprayers twice at ca 21-day intervals. A third application diluted to 1.6 g/liter was made with a portable backpack mistblower ca 21 days after the second dilute spray.

Since acephate was not registered for this type of use, little data were available on its residue behavior. An earlier study conducted under simulated eradication conditions yielded data on residues in fruit (*6*). In the present study, residues of acephate and its toxic metabolite methamidophos were determined in urban dooryard citrus foliage subjected to insecticide applications during the eradication program. Because the acute toxicity of methamidophos is much greater (acute oral LD_{50} in male rats is 21 mg methamidophos/kg compared to 945 mg acephate/kg) (*5*), residue dynamics of both compounds were assessed.

Materials and Methods

Two line transects, each along a city street, were selected in an urban area of Pompano Beach, Florida. Each transect was ca 10 city blocks long (ca 1.6 km), and

[1] Florida Agricultural Experiment Station Journal Series No. 2089. Work was supported in part by Cooperative Agreement No. 12-14-7001-1148 between the Science and Education Administration of the U.S. Department of Agriculture and the University of Florida.

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one *Citrus* spp. tree, either *C. sinensis* (orange) or *C. paradisi* (grapefruit), was selected for sampling on each city block. Although homeowner cooperation was secured in advance, there were occasional instances when samples could not be taken due to problems in gaining access to certain backyards.

The trees were sprayed by APHIS or DPI employees as part of their regular duties in the citrus blackfly eradication program. Although APHIS and DPI supervisory personnel cooperated with the residue analysis program, the persons doing the spraying were for the most part unaware of the residue sampling. This was to ensure that the monitoring would be most representative of actual eradication spraying conditions.

Each selected tree was sampled at two-week intervals, from early August until December 1978. Ten to twenty leaves were removed and placed in plastic bags. The filled bags were placed on ice and transported to the laboratory where they were stored at −25°C until analysis. Samples were stored in this manner for 0.5–3.5 months before analysis. The effect of storage on hydrolysis of acephate to methamidophos was not determined.

At the time of analysis, the leaves were thawed and 5-g aliquots were weighed. Each 5-g sample was extracted three times in a Lourdes homogenizer with 50-ml portions of ethyl acetate (150 ml total volume) and 15 g anhydrous Na_2SO_4. Resultant extracts were evaporated to dryness and dissolved in 25 ml ethyl acetate for gas chromatographic (GC) analysis. GC analysis procedures were adapted from earlier studies (*3, 4, 6*). The following instrument parameters and operating conditions were used:

Gas chromatograph:	Tracor Model 222	
Detector:	flame photometric in phosphorus mode	
Column:	glass, 91 cm long by 4 mm ID, packed with 1 percent Reoplex 400 on 80–100-mesh Gas-Chrom Q	
Temperatures:	column:	program initiated 2 minutes after injection, to increase from 140°C to 190°C at 20°C/minute
	inlet:	190°C
	detector:	160°C
Gases:	nitrogen (carrier) flowing at 50 ml/minute; hydrogen at 100 ml/minute; and air at 120 ml/minute	

Calculations for decay curves for acephate and methamidophos on each sampled tree were based on time after the last treatment according to the equation:

$$y = y_o e^{bx} \qquad (1)$$

The date of the last treatment was taken from records kept by the spray crews (Gregory F. Lotorto, January 1979; Florida Department of Agriculture and Consumer Services, Ft. Lauderdale, Fla., personal communication). The decay rates were used to compute $t_{1/2}$ values for both compounds on each sampled tree when at least three detectable residues were measured after the last treatment and when the correlation coefficient for Equation 1 was at least 0.70 by the equation:

$$t_{1/2} = \frac{\ln(0.5)}{-b} \qquad (2)$$

Results and Discussion

The first detectable foliar residues of acephate and methamidophos in transect 1 were determined on two trees on August 15 and on the other seven trees by August 29 (Table 1). In transect 2, the spraying commenced slightly later; none of the trees had detectable residues on August 15 but all did by August 29 (Table 2).

TABLE 1. *Acephate and methamidophos residues in* Citrus *spp. foliage along N.E. 2nd Street, Pompano Beach, Florida—1978*

Species	Tree No.[1]	Compound	Foliar Residues, ppm Wet Weight										
			Aug. 7	Aug. 15	Aug. 29	Sept. 11	Sept. 26	Oct. 10	Oct. 24	Nov. 7	Nov. 20	Dec. 5	Dec. 19
Citrus sinensis	1–1	Acephate	ND	20.4	5.88	52.8	6.12	10.4	2.15	0.91	0.36	0.21	<0.02
		Methamidophos	ND	4.40	0.52	15.8	1.28	2.00	0.34	0.07	0.04	<0.03	<0.03
	1–3	Acephate	ND	ND	7.35	1.60	6.60	11.5	2.07	0.82	0.04	0.07	0.02
		Methamidophos	ND	ND	1.24	0.49	2.07	2.56	0.86	0.27	<0.03	<0.03	<0.03
	1–5	Acephate	ND	ND	5.60	1.42	3.97	7.80	0.67	0.12	6.42	0.39	0.16
		Methamidophos	ND	ND	1.78	0.25	0.73	0.75	0.22	0.05	1.07	0.12	<0.03
	1–9	Acephate	ND	ND	7.67	M[2]	0.60	2.22	0.44	0.16	0.02	0.17	0.02
		Methamidophos	ND	ND	1.52	M	0.20	0.32	0.12	<0.05	<0.03	0.06	<0.03
Citrus paradisi	1–2	Acephate	ND	ND	9.14	0.87	14.7	19.4	7.25	1.66	0.08	0.06	0.16
		Methamidophos	ND	ND	2.15	0.17	3.28	1.97	2.20	0.48	0.04	<0.03	<0.03
	1–4	Acephate	ND	142.5	11.4	1.01	9.65	21.6	2.67	0.63	0.03	0.07	0.02
		Methamidophos	ND	2.93	1.85	0.33	2.65	2.00	0.62	0.09	<0.03	<0.03	<0.03
	1–6	Acephate	ND	ND	9.52	41.3	1.47	7.00	1.34	0.91	0.07	0.07	<0.02
		Methamidophos	ND	ND	1.89	3.60	0.48	0.29	0.49	0.21	<0.03	<0.03	<0.03
	1–8	Acephate	ND	ND	35.3	1.68	4.04	0.69	0.09	0.39	0.01	<0.02	<0.02
		Methamidophos	ND	ND	2.40	0.38	0.84	0.11	0.12	<0.05	<0.03	<0.03	<0.03
	1–10	Acephate	ND	ND	5.54	305.1	6.30	32.7	10.30	1.60	0.76	0.61	<0.02
		Methamidophos	ND	ND	1.21	15.0	1.29	4.00	2.70	0.27	0.17	0.15	<0.03

NOTE: ND = not detected.
[1] Prefixes 1 or 2 indicate transects 1 or 2.
[2] M = sample not collected.

TABLE 2. *Acephate and methamidophos residues on* Citrus *spp. foliage along N.E. 4th Street, Pompano Beach, Florida—1978*

Species	Tree No.[1]	Compound	Foliar Residues, ppm Wet Weight								
			Aug. 15	Aug. 29	Sept. 11	Sept. 26	Oct. 10	Oct. 24	Nov. 7	Nov. 20	Dec. 5	Dec. 19
Citrus sinensis	2–1	Acephate	ND	4.53	3.49	20.1	12.2	2.42	0.24	0.07	0.09	0.04
		Methamidophos	ND	0.11	1.25	1.90	1.64	1.20	0.12	<0.02	<0.03	<0.03
	2–4	Acephate	ND	302.5	M[2]	3.85	0.13	0.04	0.15	0.09	0.03	0.02
		Methamidophos	ND	11.00	M	1.20	0.03	0.04	0.12	0.06	<0.03	<0.03
	2–5	Acephate	ND	7.14	0.68	6.00	11.3	0.29	0.12	0.07	0.02	<0.02
		Methamidophos	ND	1.20	0.25	1.55	1.29	0.07	<0.03	<0.02	<0.03	<0.03
Citrus paradisi	2–2	Acephate	ND	M	7.72	34.8	8.44	3.07	0.14	0.19	0.07	0.10
		Methamidophos	ND	M	1.18	2.68	1.59	0.97	0.05	<0.02	<0.03	<0.03
	2–3	Acephate	ND	M	1.39	1.83	13.8	3.86	2.15	0.23	0.08	<0.02
		Methamidophos	ND	M	0.32	0.43	2.22	0.59	0.49	<0.02	<0.03	<0.03
	2–6	Acephate	ND	12.3	1.07	13.7	1.06	2.50	0.11	0.18	0.08	<0.02
		Methamidophos	ND	2.17	0.24	1.83	0.22	0.58	0.03	0.05	<0.03	<0.03
	2–7	Acephate	ND	9.93	1.01	3.69	15.8	2.36	0.11	0.14	<0.02	0.02
		Methamidophos	ND	1.86	0.25	1.45	0.63	0.48	0.05	<0.02	<0.03	<0.03
	2–8	Acephate	ND	137.8	8.01	5.44	1.68	3.31	0.70	1.77	0.17	<0.02
		Methamidophos	ND	6.25	1.40	2.35	0.40	1.34	0.18	0.67	0.06	<0.03
	2–9	Acephate	ND	10.7	6.08	3.56	1.85	0.25	0.05	0.05	0.14	<0.02
		Methamidophos	ND	1.91	1.14	1.12	0.33	0.10	<0.03	<0.02	0.05	<0.03

NOTE: ND = not detected.
[1] Prefixes 1 or 2 indicate transects 1 or 2.
[2] M = sample not collected.

TABLE 3. *Acephate application dates for the* Citrus *spp. trees in both transects, Pompano Beach, Florida—1978*

Tree No.[1]	Species	Application Date		
		First	Second	Third
1–1	*Citrus sinensis*	Aug. 10	Sept. 6	Sept. 28
1–3		Aug. 18	Sept. 14	Oct. 4
1–5		Aug. 17	Oct. 4	Nov. 7
1–9		Aug. 18	Sept. 12	Oct. 2
1–2	*Citrus paradisi*	Aug. 18	Sept. 14	Oct. 4
1–4		Aug. 23	Sept. 19	Oct. 6
1–6		Aug. 14	Sept. 7	Sept. 28
1–8		Aug. 24	Sept. 15	Oct. 2
1–10		Aug. 17	Sept. 11	Sept. 29
2–1	*Citrus sinensis*	Aug. 28	Sept. 15	Oct. 5
2–4		Aug. 29	Sept. 20	NS[2]
2–5		Aug. 21	Sept. 15	Oct. 5
2–2	*Citrus paradisi*	Aug. 28	Sept. 15	Oct. 5
2–3		Aug. 21	Sept. 13	Oct. 2
2–6		Aug. 23	Sept. 19	Oct. 11
2–7		Aug. 23	Sept. 19	Oct. 9
2–8		Aug. 28	Sept. 22	Oct. 13
2–9		Aug. 21	Sept. 13	Oct. 2

NOTE: Information supplied by G. L. Lotorto, Florida Department of Agriculture and Consumer Services, Fort Lauderdale, Florida.
[1] Prefixes 1 or 2 indicate Transect 1 or 2.
[2] NS = not sprayed.

With one exception, all trees in both transects were sprayed during the period August 10 to October 13 (Gregory F. Lotorto, January 1979; Fort Lauderdale, Fla., personal communication). The actual spray application dates are shown in Table 3. The one exception was tree 1-5 in transect 1, which was apparently overlooked initially by the spray crews and treated later when the oversight was detected. That tree received its third treatment on November 7 and this later treatment accounts for the apparent protraction of its residues evident in Table 1.

In most cases, acephate residues remained above 1 ppm during the two-month treatment period and for ca one month after the treatment period (Tables 1 and 2). The highest concentrations of both compounds were detected in samples taken during the first month of the treatment period, when some trees had residues exceeding 300 ppm acephate and 15 ppm methamidophos. The first month of the treatment period encompassed the two treatments applied as dilute sprays, whereas the third treatment, applied by mist-blower, produced lower residue values. This agrees with earlier work in which acephate and methamidophos were not detected in fruits of citrus plants treated by mist-blower application but were detected in fruits of trees treated with dilute sprays applied by hydraulic equipment (*6*). Apparently, the higher concentration coupled with less aqueous carrier results in less toxicant deposition on leaf surfaces as well as lower uptake into the fruit.

Residue values for both compounds measured after the last of the series of three treatments were used to assess the rates of decay on foliage (Table 4). The average half-lives of acephate and methamidophos on citrus foliage were 8.93 days and 8.40 days, respectively, with no pronounced difference between the two plant species. These values can be compared with half-lives of 10.3 days and 10.5 days for acephate and methamidophos, respectively, in the rind of oranges, grapefruit, lemons, and tangerines, and half-lives of 15.0 days and 6.1 days for acephate and methamidophos, respectively, in citrus pulp (*6*). In contrast, half-lives of acephate and methamidophos in needles of Douglas fir (*Pseudotsuga menziessii*) were reported in one study to be ca three days for each compound (*10*) and in another study, ca five days for each compound (*9*). In all of the above-mentioned studies as in the present study, only acephate was applied, and methamidophos residues, when de-

TABLE 4. *Decay dynamics of acephate and methamidophos on urban dooryard* Citrus *spp. trees, Pompano Beach, Florida—1978*

Tree No.[1]	Species	Acephate $t_{1/2}$, Days	Acephate N	Acephate r	Methamidophos $t_{1/2}$, Days	Methamidophos N	Methamidophos r
1-1	*Citrus sinensis*	−9.90	5	−0.98	−6.98	4	−0.98
1-3		−7.67	4	−0.88	[2]	2	[2]
1-5		−5.31	3	−0.96	[2]	2	[2]
1-9		−11.50	5	−0.75	[2]	2	[2]
2-1		−8.63	6	−0.93	−7.67	3	−0.92
2-4		−13.80	7	−0.79	[2]	5	−0.50
2-5		−6.90	5	−0.93	[2]	2	[2]
		$\bar{x}$ = −9.10			$\bar{x}$ = −7.29		
		SD = 2.89			SD = 0.54		
1-2	*Citrus paradisi*	−8.63	6	−0.90	−6.90	4	−0.91
1-4		−6.27	5	−0.94	−6.27	3	−0.99
1-6		−7.67	5	−0.96	[2]	3	−0.38
1-8		−8.63	4	−0.76	[2]	2	[2]
1-10		−8.63	5	−0.96	−9.86	5	−0.93
2-2		−9.86	6	−0.89	−5.75	3	−0.92
2-3		−6.90	5	−0.98	−13.80	3	−0.92
2-6		−9.86	4	−0.81	−7.67	3	−0.79
2-7		−5.31	4	−0.94	−7.67	3	−0.91
2-8		−11.50	4	−0.81	−11.50	4	−0.76
2-9		−13.80	5	−0.71	[2]	2	[2]
		$\bar{x}$ = −8.82			$\bar{x}$ = −8.68		
		SD = 2.41			SD = 2.81		
	Grand mean	$\bar{\bar{x}}$ = −8.93			$\bar{\bar{x}}$ = −8.40		
		SD = 2.52			SD = 2.55		

NOTE: Correlation coefficients (r) for the decay equation $y = y_0 e^{bx}$ were computed when the number of data points (N) after the last treatment was equal to or greater than 3. Half-life values for each tree ($t_{1/2}$) were computed when $r \geq 0.70$.

[1] Prefixes 1 or 2 indicate transect 1 or 2.

[2] Value not computed. See text for explanation.

tected, were presumed to be the result of hydrolysis of acephate.

In the data shown in Tables 1 and 2, a total of 114 samples contained measurable residues of both acephate and methamidophos. Twenty-nine contained acephate only (generally at levels approaching the limits of detection), and the remainder did not contain any measurable residues of either compound. Since the conversion of acephate to the more toxic methamidophos is a potential environmental problem, attention was given to the relative proportions of each compound expressed as a function of the total residue in each sample (Table 5). On the average, 81 percent of the total residue (acephate plus methamidophos) was in the form of acephate, with an average of 19 percent methamidophos. There were no pronounced differences between citrus species or between plots (Table 5), and the variability was quite low (SD $<<\bar{x}$).

Although there is significant conversion of acephate to its more toxic metabolite, methamidophos, in *Citrus* spp. leaves, the rapid disappearance of both compounds can reduce risk of exposure to dangerous levels of toxicant.

TABLE 5. *Average composition of total residue (acephate plus methamidophos) expressed as either compound, based on residues listed in Tables 1 and 2*

Species	Transect	Acephate $\bar{x}$	Acephate SD	Acephate N	Methamidophos $\bar{x}$	Methamidophos SD	Methamidophos N
Citrus sinensis	1	0.81	0.06	27	0.19	0.06	27
	2	0.77	0.14	17	0.23	0.14	17
Citrus paradisi	1	0.82	0.10	33	0.18	0.10	33
	2	0.81	0.07	37	0.19	0.07	37
Total		0.81	0.09	114	0.19	0.09	114

Acknowledgments

We gratefully acknowledge the technical assistance of Joseph A. Fiore, Susan L. Gould, Martha Johnson, June Mayor, Guy Nelson, and Robert K. Zumstein. We thank Gregory F. Lotorto of the Florida Department of Agriculture and Consumer Services for supplying data on spray application schedules. We also thank the residents along N.E. Second Street and N.E. Fourth Street, Pompano Beach, Florida, for cooperation with our sampling program. We are grateful to H. G. Bashman, T. K. Broschat, R. V. Dowell, H. N. Nigg, C. A. McDaniel, and A. Selhime for critically reviewing the manuscript.

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FISH, WILDLIFE, AND ESTUARIES

Organochlorine Residues in Eggs of Loggerhead and Green Sea Turtles Nesting at Merritt Island, Florida—July and August 1976

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ABSTRACT

Eggs from nine clutches of loggerhead turtles (Caretta caretta) *and two clutches of green turtles* (Chelonia mydas) *were collected as they were laid on Merritt Island, Florida. Eggs were incubated, frozen, and analyzed for organochlorines.*

Levels of DDE and PCB, the major contaminants, averaged less than 0.08 ppm in loggerhead eggs and were even lower in green turtle eggs. These concentrations are far below levels thought to be potentially harmful. Loggerhead eggs were frozen after 43–52 days incubation; both DDE and PCB declined significantly during this interval. Authors estimate that DDE averaged about 0.2 ppm in loggerhead eggs when they were laid.

DDE levels in eggs of both turtle species were less than levels in eggs of crocodiles (Crocodylus acutus) *from Everglades National Park and in eggs of 13 species of aquatic birds nesting on Merritt Island. The remarkably low residues in the turtle eggs probably indicate that, when not nesting, the turtles live and feed in areas remote from Florida.*

Introduction

Declining populations of marine turtles throughout the world are attributable to the taking of both adults and eggs for sale or for immediate consumption as food (*3*). In the United States, human destruction of nesting beaches and predation on eggs by raccoons (*Procyon lotor*) are also major factors (*3*). Both loggerhead (*Caretta caretta*) and the green turtle (*Chelonia mydas*) have been classified recently as "threatened," and the Florida breeding population of the green turtle has been listed as "endangered" (*11*).

Whether chemical pollution threatens marine turtles is uncertain. Eggs of the predominantly herbivorous green turtle from Ascension Island contain only very low organochlorine residues (*10*). Residues in eggs of the more carnivorous loggerhead turtle from Georgia and South Carolina appear to be somewhat higher (*8*), but data are presented in such a way that precise comparisons are not possible. The present study examined eggs of loggerhead and green turtles collected in Florida.

Materials and Methods

Entire clutches from nine loggerhead and two green turtles were collected as they were laid on the Canaveral National Seashore and the adjacent Merritt Island National Wildlife Refuge (MINWR), Brevard County, Florida. All 11 clutches were laid between July 13 and August 6, 1976. Clutch size averages more than 100 eggs in both species (*6*). At laying, 20 eggs from each loggerhead clutch and five from each green turtle clutch were selected randomly, weighed, and numbered using India ink so that toxicant levels measured later could be related to original weights of eggs. Each clutch was placed in a plastic container, covered with sand, and incubated in a laboratory (house trailer) which was open to the ambient temperature and humidity of the beach.

Clutches were dug up after intervals of 43, 45, 48, 49, or 52 days. The numbered eggs were weighed again, wrapped individually in aluminum foil, sealed in plastic bags, and frozen. The remainder of each clutch was incubated until all viable eggs had hatched; these hatchlings were released to the ocean. Eggs that did not hatch (3–10 per loggerhead clutch, 8 and 13 for green turtle clutches) were placed with others from the same clutch that had been frozen previously. Eggs were frozen after a 43–52-day incubation period because, after that length of time, eggs with living embryos could be easily distinguished from eggs in which no embryo had developed. The experimental design called for comparison of residue levels in fertile and infertile eggs.

All eggs were packed in Dry Ice and shipped to the Patuxent Wildlife Research Center (PWRC) where they were weighed and opened, and the straight-line carapace

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length of each embryo was measured with a vernier caliper. Contents of each egg minus the shell were placed in separate, tared glass jars that had been cleaned with acetone and hexane, and the jars and contents were weighed. Subsequently, each sample egg was homogenized in a blender and analyzed for organochlorines.

Loggerhead eggs frozen after 43–52 days of incubation either contained well developed embryos (mean embryo carapace lengths of samples from nine clutches ranged from 32.3 mm to 37.4 mm) or showed no embryonic development and were classified as infertile. The rate of infertility in each 20-egg sample ranged from 5 percent to 25 percent (1–5 eggs) and averaged 12 percent. All 10 green turtle eggs frozen after 43–52 days of incubation contained large embryos. Carapace lengths averaged 37.6 mm and 39.2 mm for the two clutches.

Unhatched loggerhead eggs frozen after viable eggs had hatched also either contained large embryos or were infertile. Percentages of infertile eggs were higher, ranging from 33 percent to 100 percent and averaging 69 percent. Unhatched green turtle eggs frozen after viable eggs had hatched were 90 percent and 100 percent infertile.

To make a statistical comparison of residue levels in fertile versus infertile loggerhead eggs, authors randomly selected and analyzed 10 fertile eggs from among the 20 per clutch that were frozen after 43–52 days of incubation. Then, for comparison, authors analyzed all infertile eggs from that same clutch plus all available infertile eggs frozen after the rest of the clutch hatched to a maximum combined total of 10 eggs. Green turtle clutches were treated similarly except that only five fertile eggs were analyzed from each clutch.

At an analytical sensitivity of 0.1 ppm for organochlorine pesticides and 0.5 ppm for polychlorinated biphenyls (PCBs), 107 of 170 loggerhead eggs (63 percent) and all 28 green turtle eggs contained no measurable residues. Among loggerheads, samples from three clutches contained no measurable residues, samples from two clutches had only one egg with residues, and the sample from one clutch had only three eggs with residues. Measurable residues were limited to DDE and PCB. Authors analyzed a second subsample from one fertile egg of each clutch at a sensitivity of 0.005 ppm for organochlorine pesticides and 0.025 ppm for PCBs. Residues discussed hereafter are from these 11 more sensitive analyses unless indicated otherwise.

For each analysis, a 10-g portion of the homogenized egg was mixed with anhydrous sodium sulfate and extracted for 7 hours in a Soxhlet apparatus. Extraction, sample cleanup, and separation of organochlorine pesticides from PCBs were performed as described by Cromartie et al. (*5*), except that the SilicAr separation was collected in four fractions to facilitate separation of endrin and dieldrin. The fractions were analyzed on a Hewlett-Packard Model 5753 gas-liquid chromotograph equipped with a ^{63}Ni detector, automatic sampler, and computing integrator. Instrument characteristics and operating conditions follow:

Column:	glass, 1.83 meters, packed with a mixture of 1.5 percent OV-17 and 1.95 percent QF-1	
Temperatures:	column	200°C
	detector	300°C
	injection port	250°C
Carrier gas:	5 percent methane in argon flowing at 60 ml/minute; purge flow, 40 ml/minute	

Samples were analyzed for *p,p'*-DDE, *p,p'*-TDE, *p,p'*-DDT, dieldrin, endrin, heptachlor epoxide, mirex, oxychlordane, *cis*-chlordane, *trans*-nonachlor, *cis*-nonachlor, hexachlorobenzene (HCB), toxaphene, and PCBs. Recovered PCB always resembled Aroclor 1260.

Average percentage recoveries from spiked chicken (*Gallus gallus*) egg tissue ranged from 83 percent to 104 percent. Residue data were not adjusted on the basis of these recoveries. Authors confirmed residues in one of the 11 samples analyzed at high sensitivity, using a Finnigan Model 4000 gas-liquid chromatograph–mass spectrometer in the selective ion mode.

Geometric means and 95 percent confidence intervals are given for residues because the data were positively skewed, but they were calculated only for those residues (DDE and PCB) that occurred in a majority of samples in a series. Arithmetic means and standard errors are also given where comparison with similarly derived means from other studies is required.

Results and Discussion

GENERAL LEVELS OF RESIDUES

Residues of eight organochlorine compounds were recovered from eggs of loggerhead turtles, but only DDE and DDT were found in eggs of the green turtle (Table 1). Green turtle eggs from Ascension Island contained

TABLE 1. *Organochlorine residues in nine loggerhead and two green turtle eggs from Merritt Island National Wildlife Refuge, Florida—July and August 1976*

Chemical	Number with Residues	Residues, ppm Wet Weight		
		Geometric Mean	95% CI	Range
LOGGERHEAD TURTLE EGGS				
DDE	9	0.047	0.024–0.090	0.018–0.200
DDT	2			ND–0.048
Dieldrin	4			ND–0.028
Heptachlor epoxide	2			ND–0.006
Oxychlordane	2			ND–0.017
trans-Nonachlor	1			ND–0.009
Mirex	1			ND–0.005
PCB (Aroclor 1260)	9	0.078	0.047–0.130	0.032–0.201
GREEN TURTLE EGGS				
DDE	1			ND–0.005
DDT	1			ND–0.042

NOTE: CI = confidence interval; ND = not detected.

only DDE and PCB residues (*10*). In an unspecified number of loggerhead eggs from Georgia and South Carolina, ΣDDT ranged from 0.058 ppm to 0.305 ppm and dieldrin from a trace to 0.056 ppm; embryos apparently were not observed (*8*). These latter results seem similar to the present results, but precise comparisons are not possible.

LEVELS OF DDE AND PCB COMPARED TO DAYS OF INCUBATION

Even though the range of incubation periods for loggerhead clutches was only nine days (43–52 days of incubation) the concentrations of DDE and PCB declined significantly during this time (Fig. 1). Residue data were also plotted as total micrograms per egg and as ppm wet weight of the whole egg at laying to avoid the possibility of confusing dilution through the uptake of water by the egg with actual loss of residues; significant regressions similar to Figure 1 were obtained: total μg DDE, $r = -0.743$, $0.05 > P > 0.02$; total μg PCB, $r = -0.850$, $0.01 > P > 0.001$; ppm DDE at laying, $r = -0.747$, $0.05 > P > 0.02$; ppm PCB at laying, $r = -0.790$, $0.02 > P > 0.01$. Uptake of water during this 10-day portion of incubation was probably negligible because there was no significant increase in egg weights.

Authors believe that DDE and PCB declined because a portion of these compounds present at laying was metabolized by the developing loggerhead embryos to compounds not measured by the analytical methods. Such metabolism (DDE to DBP, or 4,4′-dichlorobenzophenone) has been demonstrated in developing chicken embryos (*1*). If the linear relationships in Figure 1 are extrapolated backward, then mean levels at laying can be estimated at ca 0.9 ppm. However, because embryos metabolize the stored fat, and hence the DDE and PCB, of the egg more rapidly as they become larger and their needs become greater, the relationships of Figure 1 would not be linear over the entire incubation period. That is, the 10-day interval shown in Figure 1 constitutes 15.5 percent of the incubation period; complete incubation averaged 64.5 days (S. Vehrs, 1979, MINWR; personal communication). But the amount of metabolism during the 10 days must have been greater than 15.5 percent. Thus the amount of DDE in eggs at laying must have been less than 0.9 ppm.

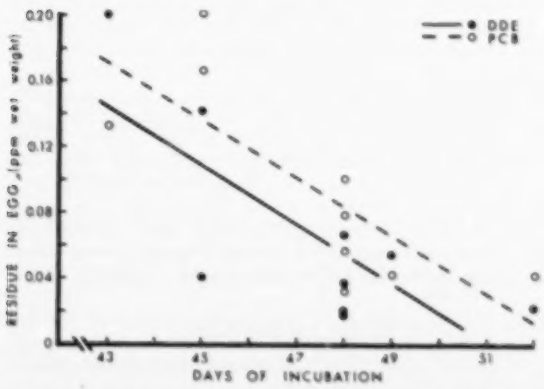

FIGURE 1. *Relationship of residue concentration to length of incubation period among nine loggerhead turtle eggs, each from a different clutch. For DDE,* $r = -0.753$, $0.02 > P > 0.01$; *and for PCB (Aroclor 1260),* $r = -0.772$, $0.02 > P > 0.01$.

To estimate DDE levels in loggerhead eggs at laying, authors used quantifications from infertile eggs because no DDE could have been metabolized. Infertile eggs were analyzed only at the 0.1 ppm sensitivity, so authors selected the three clutches in which DDE was quantified for all eggs in order to assure the most accurate analytical readings. Authors calculated arithmetic means for the infertile eggs in those clutches. The results were 0.252 ± 0.026 ppm ($n = 10$); 0.268 ± 0.057 ppm ($n = 5$); and 0.222 ± 0.040 ppm ($n = 4$). Because these means are an upwardly biased estimate of levels at laying (results are from the three most contaminated clutches), authors believe the actual value was somewhat lower, perhaps ca 0.2 ppm.

DDE LEVELS IN SEA TURTLE EGGS FROM FLORIDA COMPARED WITH DDE LEVELS IN EGGS OF CERTAIN OTHER POPULATIONS

DDE is well known for its adverse effect on the reproduction of several bird species. However, the lowest concentration in eggs known to affect the brown pelican (*Pelecanus occidentalis*), which may be the most sensitive species, is 2.5 ppm (*2*). DDE concentrations in the Florida sea turtle eggs are far below this level (Table 1).

The level of DDE in green turtle eggs in the present study was very similar to that reported for green turtle eggs from Ascension Island (Table 2). However, the eggs from Ascension contained no embryos visible to the naked eye (N. Thompson, 1979, University of Florida, Gainesville, Fla.; personal communication). If eggs in the present study had been analyzed at a similar early stage of development, DDE levels would probably have exceeded those in Ascension Island eggs.

Loggerhead eggs contained substantially more DDE than did green turtle eggs (Table 2). When we consider

TABLE 2. *Residues of DDE in eggs from five reptile and bird populations*

Population	*n*	DDE, ppm Wet Weight: Arithmetic Mean ± SE	DDE, ppm Wet Weight: Range	Ref.
Loggerhead turtle (Florida)	9	0.066 ± 0.021	0.018–0.200	Present study
Green turtle (Florida)	2	0.002 ± 0.002	ND–0.005	Present study
Green turtle (Ascension Island)	10	0.003 ± 0.001	ND–0.009	(*10*)
Crocodile (Florida)	23	1.19 ± 0.15	0.28–3.2	(*7*)
White ibis (Florida)	10	0.29 ± 0.08	ND–0.84	(*9*)

NOTE: SE = standard error; ND = not detected.

the reductions that have probably occurred due to incubation of the Florida eggs, the data in Table 2 suggest that both the contrasting food habits of the two species and the different geographic locations (Ascension Island and Florida) affected DDE levels. The difference in nesting location is related to differences in primary feeding locations. When not nesting, the Ascension Island turtles feed along the Atlantic coast of Brazil (*4*). No one knows where the Florida turtles feed when not nesting, but if organochlorine pollutants in their food species near Florida are high, these pollutants could produce levels in their eggs that exceed levels in eggs from turtles that feed near Brazil.

Eggs of crocodiles (*Crocodylus acutus*) from Everglades National Park contained no visible embryos when prepared for chemical analysis (*7*). DDE concentrations in these eggs (Table 2) were about six times greater than DDE concentrations estimated to have been in loggerhead eggs at laying. The loggerhead eggs had lower DDE residues even though both species are large, carnivorous, marine-estuarine reptiles found in Florida.

Eggs of Florida sea turtles also contained lower residues than did eggs of aquatic birds nesting on MINWR. Eggs of the white ibis (*Eudocimus albus*) contained the lowest DDE residues (Table 2) among 13 species of aquatic birds whose eggs were collected at MINWR (*9*). Most of the white ibis eggs contained small embryos, but the only two with feathered embryos contained 0.12 ppm and 0.18 ppm DDE and three showing no embryonic development contained 0.50, 0.34, and 0.84 ppm DDE (H. Ohlendorf, 1979, PWRC; personal communication). Thus DDE levels in white ibis eggs with large embryos exceeded levels in turtle eggs with large embryos (Table 2), and DDE levels in white ibis eggs showing no embryonic development exceeded levels estimated to have been present in loggerhead eggs at laying.

In summary, the residue concentrations in loggerhead and green turtle eggs from Florida are remarkably low. These low levels probably reflect low dietary intake. The importance of this factor is suggested by the difference in DDE levels in eggs between the two species. Furthermore, the relatively low residue levels in turtle eggs in the present study compared with eggs of crocodiles and aquatic birds probably indicate that when not nesting the turtles live in areas remote from Florida. Such a pattern, with primary feeding sites and nesting sites distant from each other, is common among sea turtles (*3*).

Acknowledgments

We thank J. Baker of MINWR for suggesting that we undertake this study, L. Ehrhart of Florida Technological University for providing the turtle eggs, and S. Vehrs of MINWR for information about sea turtles at MINWR. We are grateful to G. Chasko for preparing the eggs for analysis. We thank the National Aeronautics and Space Administration for permitting the collection of eggs and for flying them to Washington, D.C. Finally, we thank E. Dustman and R. Hall for critical reviews of the manuscript.

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Accumulation of Polychlorinated Biphenyls in American Shad During Their Migration in the Hudson River, Spring 1977

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ABSTRACT

Fifty-two female American shad (Alosa sapidissima) *were collected during the spring of 1977 at two sites on the lower Hudson River, 27 miles and 75 miles from the river mouth. The fish were extracted with hexane, and the extracts were analyzed by electron-capture gas chromatography (EC-GC) and by GC/mass spectrometry (MS). PCBs were quantitated by EC-GC, and the concentrations were compared by fish length and by site. Fish collected from the downstream site contained a mean PCB concentration of 2.0 ± 1.0 μg/g, wet weight; fish from the upstream site contained a mean PCB concentration of 6.1 ± 2.6 μg/g, wet weight. Aliquots of the hexane extracts were fractionated before analysis by GC/MS. The presence of PCBs was confirmed, and DDE and the alkane series from C_{21} through C_{34} were detected. American shad are saltwater fish that only enter fresh water to spawn. Because they do not feed in fresh water before spawning, they may be used as an indicator of water contamination.*

Introduction

Toxic trace contaminants such as polychlorinated biphenyls (PCBs) permeate the Hudson River (*6*). There are several methods available to monitor this contamination, involving the collection of various samples, such as water, sediments, plants, turtles, macroinvertebrates, fish, and aquatic mammals. For the present study, migratory fish were chosen. American shad (*Alosa sapidissima*) are saltwater fish that enter fresh water only to spawn. They do not eat in fresh water before spawning (*4*); therefore any contamination enters their bodies directly from the water.

This paper presents the results of analyses of fish collected during the spring of 1977. Quantitative results for PCBs are reported, and other compounds are identified.

Sampling and Analysis

SAMPLE PREPARATION

Fifty-two female shad were collected by the New York State Department of Environmental Conservation (DEC) at two sites on the Hudson River and were tagged with an identification number. Twenty were from a site near the Tappan Zee Bridge, and 32 were from a site at Poughkeepsie (27 miles and 75 miles, respectively, from the river mouth), as indicated in Figure 1. Each fish was scaled, beheaded, definned, deboned, gutted, and then homogenized in a Model CFP5 Cuisinart food processor. A 5.0-g subsample from each fish was frozen and lyophilized for 12 hr, and then extracted with 100 ml hexane in a Soxhlet extractor for 2 hr. The extract was quantitatively transferred to a Kuderna-Danish apparatus and concentrated to about 5 ml. The

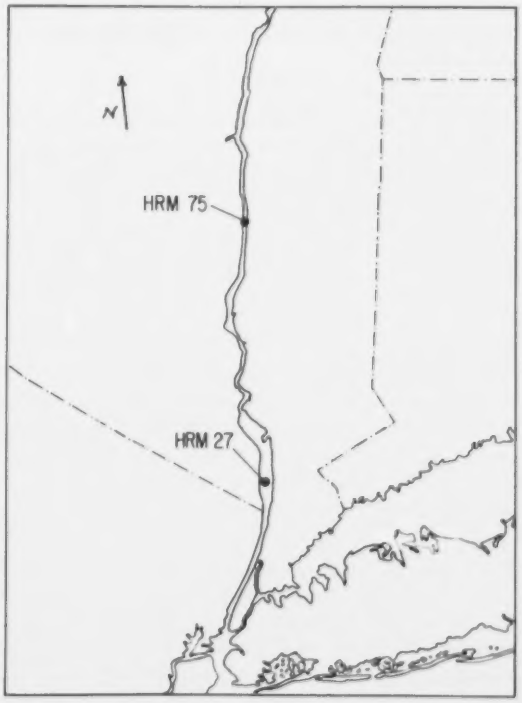

FIGURE 1. *Map of Hudson River sampling sites, for American shad, spring 1977.*

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[2] Division of Laboratories and Research, New York State Department of Health, Albany, N.Y. 12201.

concentrate was diluted to 10.0 ml of which 2.0 ml was used for electron-capture gas chromatography (EC–GC) and 8.0 ml was used for GC/mass spectrometry (MS). All of the fish were subjected to EC–GC analysis, and 25 were further analyzed by GC/MS.

CLEANUP

A 2.0-ml aliquot of extract for each fish was passed through a column containing 10.0 g of 2 percent deactivated 60–100-mesh Florisil topped with 2.0 g sodium sulfate. The Florisil was activated by heating at 450°C for 4 hr and was cooled in a desiccator. Fifty-gram aliquots were placed in an Erlenmeyer flask which was mounted on a wrist-action shaker. While the flask was shaken at low speed, 1.0 ml distilled-deionized water was added dropwise. Shaking was continued at high speed for 30 min. The aliquots of 2 percent deactivated Florisil were stored in glass jars which were sealed with Teflon lids. Purity was checked by placing 10.0 g of the combined batches in a glass column and eluting the column with 50 ml hexane. The eluate was collected and concentrated to 1.5 ml in a Kuderna-Danish apparatus, and then analyzed by electron-capture GC as described for the sample analysis.

The extract-charged column was eluted with ca 50 ml hexane, and the first 40 ml of eluate was collected. PCBs are eluted with this volume, but more polar compounds, such as DDT and triglycerides, are retained on the column (*5*). The eluate was concentrated in the same manner as the extract, and diluted to a final volume of 1.5 ml, which was transferred to a 2-ml Wheaton GC vial for analysis.

GC ANALYSIS

GC analysis was performed on a Hewlett-Packard Model 5840A digital gas chromatograph equipped with a ^{63}Ni electron-capture detector and a Model 7617A automatic sampler.

Instrument parameters and operating conditions were as follows:

Column:	glass, 6 ft long by 2 mm ID, packed with 1 percent Apiezon L on 100–120-mesh Supelcoport	
Injection volume:	5.0 µl	
Temperatures, °C:	injection	225
	detector	300
	oven	held 5 min at 160°C, then increased 10°C/minute to 220°C
Carrier gas:	ultra high purity argon–methane (95+5), flowing at 18 ml/minute	
Total run time:	38 minutes	

The microprocessor of the EC–GC was calibrated, using a mixture of 4 µg each of Aroclors 1016, 1221, 1254, and 1260/ml plus 0.2 µg mirex/ml. These four commercial mixtures contain the complete range of PCB homologs and isomers produced by the iron-catalyzed chlorination method (*1*). The inclusion of Aroclors with intermediate chlorine contents, such as 1232, 1242, and 1248, would have resulted in overly complicated patterns. Twenty-six peaks were resolved in the standard mixture (Fig. 2) and assigned to their Aroclors of origin (Table 1) by comparison with individual Aroclor chromatograms. The major PCB isomer component of each peak was determined using the procedure reported previously (*2*) by comparison with the retention time data of Sissons and Welti (*10, 14*) and Jensen and Sundstrom (*7*).

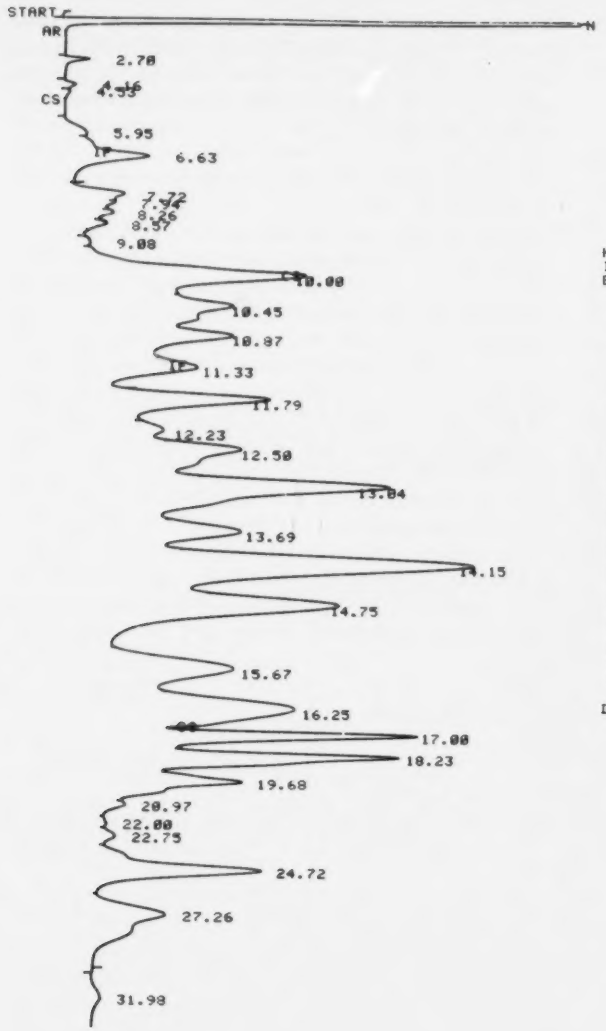
Quantitation was effected on a peak-to-peak basis. Eleven individual homologs, denoted in Table 1, were each analyzed at range of concentrations (0.5–4.0 µg/ml) in order to calculate a response factor. The response factors were normalized as area (integrator counts)/concentration (0.1 µg/ml). The logarithm of the average response factors for each group of isomers (i.e., the same number of chlorine atoms per molecule) was graphed versus the chlorine number (Fig. 3). The resulting curve was nearly linear (correlation factor $\rho = 0.95$). Analysis by the method of least squares (*9*) yields a straight line which was used to estimate response factors for the remainder of the peaks in the standard mixture. These factors were programmed into the GC microprocessor, and the resulting amounts calculated by the microprocessor were summed and compared to the true value of the standard solution. Standard solutions of each of the four Aroclor mixtures were also analyzed. By use of an iterative approach, the response factors were adjusted, the microprocessor was reprogrammed, and the standard solutions were reanalyzed.

Recovery studies were performed by separately spiking 5.0-g (wet weight) portions of uncontaminated fish

TABLE 1. *Peak assignments for PCB standard, 4 µg/ml each of Aroclors 1016, 1221, 1254, and 1260*

Retention Time, Min.	Cal No.	µg/ml in 16 µg/ml 1221, 1016, 1254, 1260 (1:1:1:1)	Major Component of Peak	Major Contributing Aroclor Mixture
2.73	2	1.47	2*	21
4.21	3	1.55	2,2'*†+4*†	16 + 21
6.64	4	1.46	2,4'*	16 + 21
7.78	5	0.53	2,2',5'*†	16 + 21
8.30	6	0.48	2,2',4'	16
8.63	7	0.42	2,2',3'	16 + 21
10.05	8	1.97	Cl_2	16
10.55	9	0.37	2,5,2',5'*+2,3,2',5'*†	16 + 54
10.95	10	0.25	2,3,2',3'*†	16 + 54
11.41	11	0.17	Cl_3	16 + 54
11.89	13	0.37	2,5,2',3',6'	16 + 54 + 60
12.33	14	0.56	Cl_3	54
12.60	15	0.23	2,5,3',4'*	16 + 54
13.19	16	0.33	2,5,2',4',5'†	54 + 60
13.83	17	0.24	2,5,2',3',4'†	54 + 60
14.33	18	1.70	2,3,4,3',6'+Cl_4	54 + 60
14.96	20	0.93	2,3,6,2',4',5'	54 + 60
15.89	21	0.39	2,3,4,2',3',6'	54 + 60
16.46	22	1.12	3,4,2',4',5'	54
17.35(R)	1	0.52	2,4,5,2',4',5'*+ 3,4,2',3',4'	54
18.56	23	0.31	2,3,4,2',4',5'*	54 + 60
19.25	24	0.59	Cl_5	60
20.05	25	0.27	2,3,4,2',3',4'+ 2,3,4,2',3',4',6'	54 + 60
23.45	26	0.20	Mirex	Mirex
25.42	27	0.22	2,4,5,2',3',4',5'	60
27.93	28	0.14	Cl_5	60

NOTE: * = pure compound obtained from Analabs, Inc. (North Haven, Conn.); † = pure compound obtained from RFR Corp. (Hope, R.I.).



HP RUN # 9 JUN/25/77 TIME 23:25:04
ID: 41577 BOTTLE 9
ESTD

RT	EXP RT	AREA	CAL #	AMT
2.70	2.70	239500	2	1.452
4.16	4.15	108600	3	1.530
6.63	6.62	1090000	4	0.001
7.72	7.71	396500	5	0.542
7.94	7.93	297300	12	0.001
8.26	8.25	324300	6	0.479
8.57	8.57	283700	7	0.419
9.08	9.08	63700	19	0.001
10.00	10.00	2416000	8	1.940
10.45	10.45	1544000	9	0.370
11.33	11.33	704200	11	0.332
11.79	11.79	784200	13	0.409
12.23	12.23	193800	14	0.301
12.50	12.50	1093000	15	0.602
13.04	13.04	2439000	16	0.339
13.69	13.68	1016000	17	0.248
14.15	14.15	3521000	18	1.770
14.75	14.74	2228000	20	0.963
15.67	15.66	1250000	21	0.393
16.25	16.24	2361000	22	1.131
17.00	17.00	5470000	(R) 1	0.525
18.23	18.23	6408000	23	0.315
19.68	19.66	[illegible]	25	0.282
22.75	22.76	[illegible]	26	0.229
24.72	24.72	4193000	27	0.223
27.26	27.26	3228000	28	0.378

DIL FACTOR: 1.0000 E+ 0

FIGURE 2. *EC chromatogram of PCB standard, 4 μg/ml each of Aroclors 1016, 1221, 1254, and 1260.*

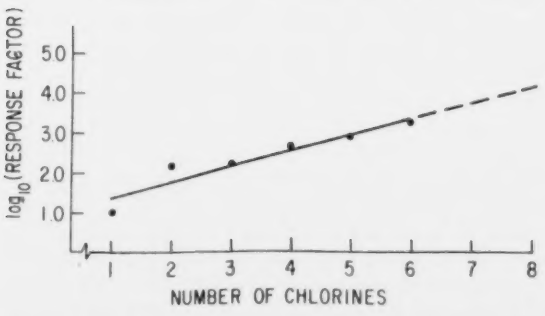


FIGURE 3. *Plot of $\log_{10}$ (response factor) versus number of chlorine atoms on biphenyl.*

homogenate with each of the four Aroclor mixtures, in triplicate. A 100-μl acetone solution of the Aroclor (100 μg/ml) was slowly added as the portion was rehomogenized, thus yielding a concentration in the spiked portion of 2.0 μg/g (wet weight) of the particular Aroclor. Each spiked portion was prepared and analyzed in the same manner as were the samples. The spike recoveries for some major peaks in the four Aroclor mixtures are reported in Table 2. All results are uncorrected for recovery.

Sample concentrations were entered into a PDP 11/45 computer which summed the concentrations and applied the dilution factors, producing a for-

TABLE 2. *Spike recoveries for some major peaks in four Aroclor mixtures*

Aroclor	Peak Component	% Recovery			
		Replicate			
		1	2	3	Average
1221	2	33	33	26	31
	2,2'+4	40	40	43	41
	2,4'	51	49	51	50
1016	2,4'	35	37	35	36
	2,2',5'	52	52	50	51
	Cl_3	77	80	78	78
	2,5,2',5'+2,3,2',5'	95	101	94	97
1254	2,5,2',5'+2,3,2',5'	79	79	79	79
	Cl_4	77	87	87	84
	2,5,2',3',6'	73	74	74	74
	2,5,3',4'	96	93	96	95
	2,5,2',4',5'	72	71	71	71
	2,3,4,2',3',6'	72	72	72	72
	2,4,5,2',4',5'+3,4,2',3',4'	65	66	66	66
	2,3,4,2',4',5'	68	68	65	67
	2,3,4,2',3',4'+2,3,4,2',3',4',6'	65	71	77	71
1260	2,5,2',3',6'	77	80	80	79
	2,5,2',4',5'	70	81	76	76
	2,3,4,2',3',6'	70	78	74	74
	2,4,5,2',4',5'+3,4,2',3',4'	66	77	69	71
	2,3,4,2',4',5'	66	73	69	69
	2,3,4,2',3',4'+2,3,4,2',3',4',6'	66	74	65	68
	2,4,5,2',3',4',5'	61	67	62	63
	Cl_6	64	71	67	67

matted report (Fig. 4). *p,p'*-DDE was estimated from the 2,5,2',3',4'-pentachlorobiphenyl peak by assuming that its ratio with the 2,5,3',4'-tetrachlorobiphenyl peak was constant at 1.05:1.00. The following formula was used:

$$\mu g\ p,p'\text{-DDE/g} = \left(A_1 - \frac{A_2}{1.05}\right) \times 0.196 \times 10^{-6}$$

Where A_1 is the area of the 2,5,2',3',4'-pentachlorobiphenyl peak; A_2 is the area of the 2,5,3',4'-tetrachlorobiphenyl peak; and the constant represents the response coefficient of the *p,p'*-DDE peak at a concentration of 1.7 μg/ml. Since the relevant PCB concentrations are usually small compared to the *p,p'*-DDE concentration, the approximation was fairly good, with a detection limit of 0.1 μg *p,p'*-DDE/ml. The residual pentachlorobiphenyl concentration was included in the sum to obtain the total PCB concentration. As a quality control, solutions designed to mimic the common concentrations of PCBs in fish were analyzed frequently to test detector and integrator responses. These quasi-fish contained 4 μg Aroclor 1016/ml, 8 μg 1254/ml, 4 μg 1260/ml, and 0.33 μg mirex/ml. The detection limit was 0.5 ng total PCB, which corresponds to 0.2 μg/g (wet wt) in the fish.

SAMPLE: 4:4:4:4 (1016:1221:1254:1260) PCB STND

-PEAK-	-COMPONENT-	-AMOUNT (PPM W/W)-
1	2,4,5,2',4',5' & 3,4,2',3',4'	.525
2	2	1.452
3	2,2' & 4	1.530
4	2,4'	.801
5	2,2',5'	.542
6	2,2',4'	.476
7	2,2',3'	.419
8	CL3	1.940
9	2,5,2',5' & 2,3,2',5'	.370
11	CL4	.332
13	2,5,2',3',6'	.409
14	CL4	.301
15	2,5,3',4'	.602
16	2,5,2',4',5'	.339
17	2,5,2',3',4'	.248
18	2,3,4,3',6' & CL6	1.770
20	2,3,6,2',4',5'	.963
21	2,3,4,2',3',6'	.393
22	3,4,2',4',5'	1.131
23	2,3,4,2',4',5'	.315
25	2,3,4,2',3',4' & 2,3,4,2',3',4',6'	.282
26	MIREX	.229
27	2,4,5,2',3',4',5'	.223
28	CL8	.378
	TOTAL	15.970

FIGURE 4. *Computer output for PCB standard, 4 μg/ml each of Aroclors 1016, 1221, 1254, and 1260.*

GAS CHROMATOGRAPHY/MASS SPECTROMETRY

The 8.0-ml aliquots of extracts for 13 shad from each site were pooled to form two samples, which were concentrated to 25 ml. For each composite sample, 13 columns containing 10.0 g of 2 percent deactivated Florisil and 2.0 g sodium sulfate were set up. Two ml of the concentrated composite was applied to each column and eluted with hexane. Forty ml of eluate was collected from each column, recombined, and concentrated to 2 ml. After the initial cleanup, the final 2 ml was passed through a column containing 10.0 g activated Florisil and 2.0 g sodium sulfate, and eluted with hexane. Ten 5-ml fractions were collected and each was concentrated to 0.1 ml and analyzed separately by GC/MS.

Analyses were performed on a Finnigan gas chromatograph/mass spectrometer/Data System Series 9500/1015D/6000. Instrument parameters and operating conditions were as follows:

Gas chromatograph:	
injection volume	5 µl
column	glass, 5 ft long by 2 mm id packed with 2 percent Apiezon L on Ultrabond
temperature	190°C
Mass spectrometer:	
ionization energy	70 eV
emission current	400 µamp
pre-amp sensitivity	10^{-6} amp/volt
instrument range	H
Data system:	
mass range	100–500
integration time	10
seconds per scan	4

The detection limit was 5 ng 2,4′-dichlorobiphenyl and 200 ng Aroclor 1254.

Results

Table 3 lists the quantitative results of EC–GC for PCBs. Because the correlation between length and PCB concentration was investigated, the lengths of the shad are also listed. Those fish with a PCB concentration or a length different by more than 2 SD from the mean were excluded from further computations, and the means were recalculated. Mean PCB concentrations from the two sites were compared using Student's *t*-test, assigning a significance level of 1 percent and without assuming equal variability of the two groups (9). The lengths were treated in a similar manner. Both were found to differ. The mean PCB concentration for shad from the Tappan Zee site (HRM 27) was 2.0 ± 1.0 µg/g, wet weight, and for shad from the Poughkeepsie site (HRM 75), the mean PCB concentration was 6.1 ± 2.6 µg/g, wet weight. The mean length of HRM 27 fish was 48.2 ± 3.0 cm, and of HRM 75, 52.9 ± 4.4 cm. The average length of the upriver fish is about 10 percent greater, whereas the average PCB concentration is nearly three times higher. There is only a weak positive correlation within each group between length and PCB concentration. The coefficient for HRM 27 is +0.40, and for HRM 75, +0.50. Chromatograms of a 16-ppm standard, a 16-ppm quasi-fish, and fish No. 2C–9757 are shown in Figures 2, 5, and 6, and computer outputs for the same samples are shown in Figures 4, 7, and 8. PCB concentrations are recorded by component, as listed in Table 1. Using the algorithm described above, no *p,p′*-DDE was quantitated.

The 25 shad further analyzed by GC/MS were chosen at random and are listed in Table 4. The PCB concen-

TABLE 3. *Length of and total PCB concentration in American shad from the Hudson River, spring 1977*

HRM 27 [1]			HRM 75 [2]		
Tag No.	Length, cm	Total PCB Concn., µg/g wet wt	Tag No.	Length, cm	Total PCB Concn., µg/g wet wt
2C–9776	50.8	11.7 [3]	2C–9214	50.0	5.8
2C–9779	48.3	1.1	2C–9215	44.7	5.6
2C–9780	47.0	2.6	2C–9216	49.5	2.7
2C–9781	43.4	2.5	2C–9221	51.6	2.4
2C–9782	54.1	5.5	2C–9222	50.5	2.4
2C–9783	43.2	1.5	2C–9223	51.6	6.9
2C–9784	43.7	2.3	2C–9224	46.7	1.9
2C–9785	45.7	2.0	2C–9225	49.5	6.1
2C–9786	50.8	2.1	2C–9226	47.0	3.3
2C–9787	46.2	1.4	2C–9227	55.6	6.4
2C–9788	45.7	0.9	2C–9228	49.5	2.3
2C–9789	50.8	1.8	2C–9229	49.3	11.2
2C–9790	49.5	1.2	2C–9230	51.1	8.7
2C–9791	50.8	2.0	2C–9231	61.0	6.7
2C–9792	48.8	1.2	2C–9232	50.5	6.3
2C–9793	45.7	1.3	2C–9233	55.4	6.4
2C–9794	47.0	1.6	2C–9234	62.2	12.2
2C–9795	50.8	1.7	2C–9753	58.7	16.1 [3]
2C–9797	48.3	3.1	2C–9754	51.6	4.4
2C–9798	50.8	2.4	2C–9755	53.3	7.7
			2C–9756	54.6	7.3
			2C–9757	55.9	6.3
			2C–9758	54.6	9.0
			2C–9759	40.6 [3]	5.3
			2C–9760	54.6	7.6
			2C–9761	55.9	19.0 [3]
			2C–9762	54.6	4.3
			2C–9763	48.3	4.2
			2C–9764	56.6	9.4
			2C–9765	54.6	4.2
			2C–9766	57.2	8.6
			2C–9767	62.2	6.3
Mean ±SD	47.9 ±3.1	2.0 ±1.0	Mean ±SD	52.9 ±4.4	6.1 ±2.7

[1] Tappan Zee site, 27 miles from the mouth of the Hudson River.
[2] Poughkeepsie site, 75 miles from the mouth of the Hudson River.
[3] Over 2 SD difference.

TABLE 4. *American shad from Hudson River analyzed additionally by GC/MS, spring 1977*

HRM 27 [1]		HRM 75 [2]	
Tag No.	PCB Concn., µg/g	Tag No.	PCB Concn., µg/g
2C–9776	11.7	2C–9216	2.7
2C–9781	2.5	2C–9222	2.4
2C–9782	5.5	2C–9224	1.9
2C–9783	1.5	2C–9225	6.1
2C–9784	2.2 (twice)	2C–9228	2.3
2C–9784	2.3	2C–9229	11.2
2C–9786	2.1	2C–9754	4.4
2C–9787	1.4	2C–9755	7.7
2C–9790	1.2	2C–9756	7.3
2C–9793	1.3	2C–9757	6.3
2C–9795	1.7	2C–9759	5.3
2C–9797	3.1	2C–9761	19.0
2C–9798	2.4	2C–9767	6.3
Mean	3.0	Mean	6.4

[1] Tappan Zee site, 27 miles from the mouth of the Hudson River.
[2] Poughkeepsie site, 75 miles from the mouth of the Hudson River.

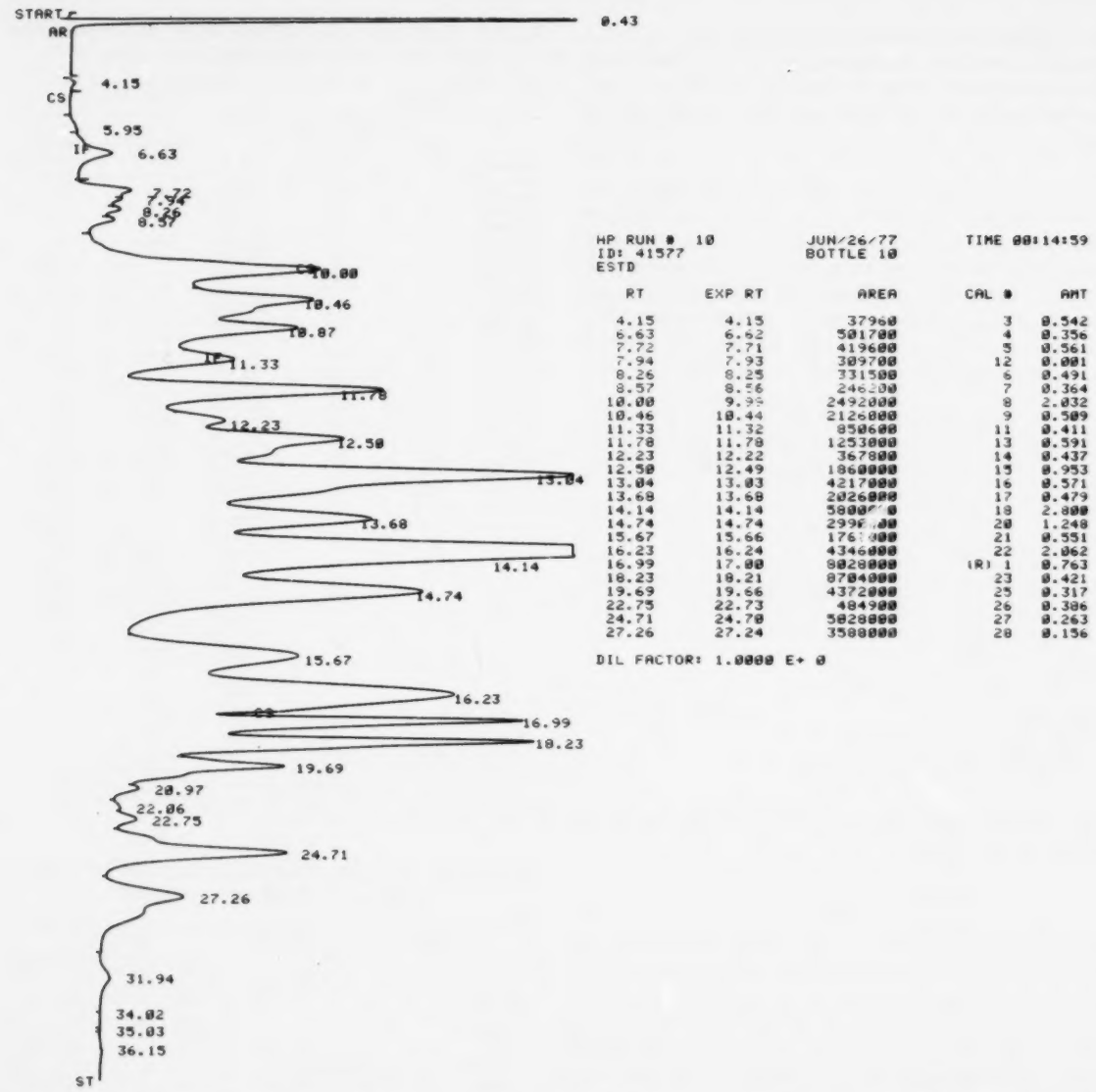
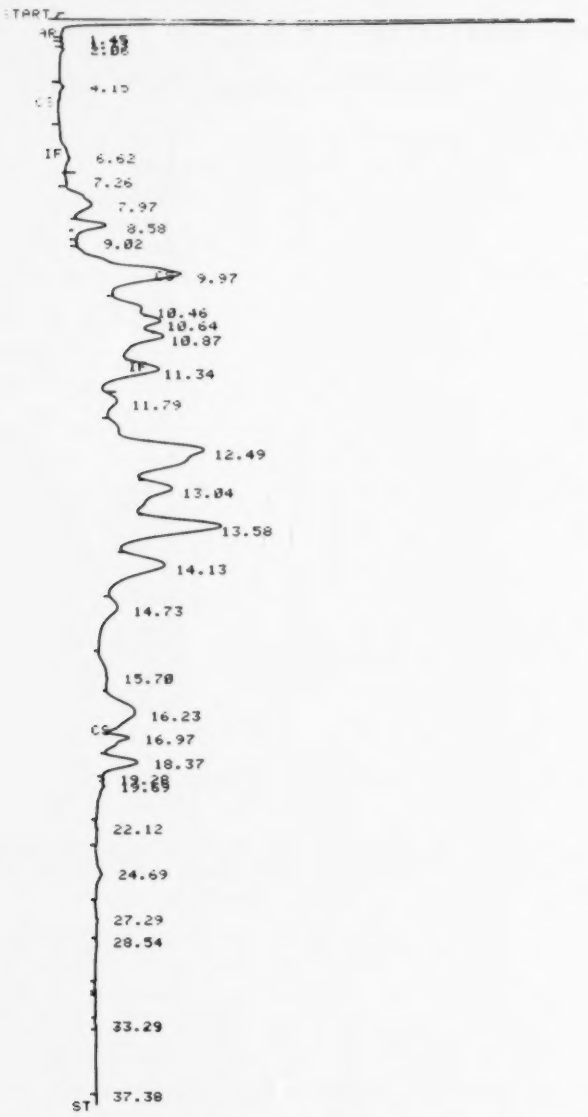


FIGURE 5. *EC chromatograms of PCB quasi-fish: 4 μg/ml each of Aroclors 1016 and 1260; 8 μg/ml Aroclor 1254; and 0.33 μg/ml mirex.*

tration mean did not differ significantly from the respective group means, as determined by the statistical test described above. The compounds identified by MS are listed in Table 5. Nonpolar compounds, which usually interfere with MS determinations of PCBs, elute first from the Florisil column. The alkane series, from C_{22} to C_{26}, were collected in fraction 1. The peaks in the total ion chromatograms (Fig. 9) are quite broad, indicating a mix of isomers for each alkane. PCBs from trichloro- through pentachloro-, were collected in fractions 3–7 (Fig. 10). Consistent with the EC–GC analysis, more PCB components were detected in the fish collected up-river. A notable exception is the polar trichlorobiphenyls detected in fraction 27–7. DDE, which is difficult to quantitate by EC–GC because it tends to overlap a PCB peak, as explained above, was only observed in the fish from HRM 75 (Fig. 11), apparently in a concentration below the EC–GC detection limit.

Discussion

Fractionation of the cleaned extract on activated Florisil aids in the analysis of fish for pesticides and PCBs. The mass spectrometer analyzing chamber does not become



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ESTD

RT	EXP RT	AREA	CAL #	AMT
4.15	4.15	117800	3	1.681
6.62	6.61	61530	4	0.044
7.97	7.92	427700	12	0.001
8.58	8.55	390800	7	0.579
9.02	9.06	51970	19	0.001
9.97	9.98	1487000	8	1.213
10.46	10.43	365300	9	0.086
10.64	10.63	429700	10	0.264
11.34	11.31	454900	11	0.220
11.79	11.76	55010	13	0.026
12.49	12.47	1218000	14	0.624
13.04	13.01	717600	16	0.097
13.58	13.66	1028000	17	0.243
14.13	14.12	651800	18	0.315
14.73	14.72	179000	20	0.075
15.70	15.64	89420	21	0.028
16.23	16.22	486700	22	0.231
16.97	17.00	618900	(R) 1	0.059
18.37	18.19	873200	23	0.042
19.28	19.30	40840	24	0.017
19.69	19.64	164700	25	0.012
24.69	24.67	169600	27	0.009
27.29	27.21	53760	28	0.002

DIL FACTOR: 1.0000 E+ 0

FIGURE 6. *EC chromatogram of American shad No. 2C-9757, Hudson River, spring 1977.*

contaminated, thus the background noise is reduced. The chromatograms are simplified; DDE does not overlap a PCB peak, which facilitates quantitation of both. If DDE were present at a higher concentration, as is the case in fish from Lake Ontario which have concentrations ranging from 1 ppm to 5 ppm (Brian Bush, 1977, personal communication), the DDE would be quantitated by the method described above.

Shad were analyzed in 1975 by DEC (*11*) during a statewide monitoring program. Fifteen shad were collected in the lower Hudson River as far upstream as Coxsackie/Catskill. The sites were not specifically identified in the report. Several of the fish samples were pooled, so that there were six composites analyzed. Results were reported in terms of the Aroclor 1242/1016 and Aroclor 1254 averages, namely 1.35 ppm and 1.14 ppm wet weight, respectively, for an overall average of 2.49 ppm. This is close to the overall average of 5.1 ppm obtained in the present study, although there is not sufficient data for full statistical comparison.

The American shad seems to be a good species of fish with which to monitor water pollution of a river system. The shad ranges throughout the eastern seaboard. It is large enough and of sufficient number to be collected easily and without impairing its population. Direct water analyses are difficult to perform. The only PCB concen-

SAMPLE: 4:8:4 (1016:1254:1260) PCB QUASI-FISH

-PEAK-	-COMPONENT-	-AMOUNT (PPM W/W)-
1	2,4,5,2',4',5' & 3,4,2',3',4'	.763
3	2,2' & 4	.542
4	2,4'	.356
5	2,2',5'	.561
6	2,2',4'	.491
7	2,2',3'	.364
8	CL3	2.032
9	2,5,2',5' & 2,3,2',5'	.509
11	CL4	.411
13	2,5,2',3',6'	.591
14	CL4	.437
15	2,5,3',4'	.953
16	2,5,2',4',5'	.571
17	2,5,2',3',4'	.479
18	2,3,4,3',6' & CL6	2.800
20	2,3,6,2',4',5'	1.248
21	2,3,4,2',3',6'	.551
22	3,4,2',4',5'	2.062
23	2,3,4,2',4',5'	.421
25	2,3,4,2',3',4' & 2,3,4,2',3',4',6'	.317
26	MIREX	.386
27	2,4,5,2',3',4',5'	.263
28	CL8	.156
	TOTAL	16.878

FIGURE 7. *Computer output for PCB quasi-fish, 4 μg/ml each of Aroclors 1016 and 1260, 8 μg/ml Aroclor 1254, and 0.33 μg/ml mirex.*

trations reported in Hudson River waters, from the Troy and Poughkeepsie areas, are in the range of 0.11–1.1 ppb (*6*) which strains the limit of detection. As mentioned in the introduction, shad do not eat in fresh water before spawning. Therefore, any contaminants they contain are due to their ocean feeding or are assimilated directly from the river water. An indication of the water contamination between the river mouth and the point of collection is obtained. This information could not be obtained as conveniently by other means.

There is a chance that the few fish having PCB concentrations significantly higher than the mean levels are repeat spawners (Ronald Sloan, 1979, DEC; private communication). Talbot (*12*) in 1954 estimated that 51 percent of the shad return to spawn again in the Hudson River. This is probably a high estimate, because in 1975 Chittenden (*3*) measured a repeat rate of only 3 percent in the Delaware River. Shad in more southern rivers spawn only once (*13*). The chance of repeat spawners did not prevent the observation of a significant increase in contamination levels in the fish collected up-river, even with only a small sampling.

In addition to the use of these fish for monitoring river contamination, the shad are important in their own right. The Hudson River shad fishery is being redeveloped. The New York State legislature, with the support of the National Oceanic and Atmospheric Administration, administered a study of the fishery (*8*). At that time, the major concerns were over-fishing and low oxygen supply in the river mouth. Those problems have been corrected, and the shad population is increasing. The annual festival held in April to celebrate the shad run has been revitalized. In July 1979, the State Environmental Conservation law was amended to establish a fishery management program for the tidal portion of the Hudson River (i.e., as far north as Troy, New York). The fish should be analyzed periodically as a check on their quality and as an indication of water quality.

SAMPLE: 2C-9757

-PEAK-	-COMPONENT-	-AMOUNT (PPM W/W)-
1	2,4,5,2',4',5' & 3,4,2',3',4'	.089
3	2,2' & 4	.020
4	2,4'	.066
7	2,2',3'	.869
8	CL3	1.819
9	2,5,2',5' & 2,3,2',5'	.132
10	2,3,2',3'	.396
11	CL4	.330
13	2,5,2',3',6'	.039
14	CL4	.936
16	2,5,2',4',5'	.146
17	2,5,2',3',4'	.365
18	2,3,4,3',6' & CL6	.473
20	2,3,6,2',4',5'	.113
21	2,3,4,2',3',6'	.042
22	3,4,2',4',5'	.347
23	2,3,4,2',4',5'	.063
24	CL7	.025
25	2,3,4,2',3',4' & 2,3,4,2',3',4',6'	.018
27	2,4,5,2',3',4',5'	.013
28	CL8	.003
	TOTAL	6.304

FIGURE 8. *Computer output for American shad No. 2C-9757, Hudson River, spring 1977.*

TABLE 5. *Identification of compounds, by fraction, found in composites of American shad from the Hudson River, spring 1977*

HRM 27 Composite [1]			HRM 75 Composite [2]		
Fraction	Scan No.	Compound	Fraction	Scan No.	Compound
27-1	60	Docosane	75-1	12	Pristane
	88	Tricosane		59	Docosane
	129	Tetracosane		85	Tricosane
	194	Pentacosane		125	Tetracosane
	286	Hexacosane		187	Pentacosane
				276	Hexacosane
27-3	47	Trichlorobiphenyl	75-3	50	Tetrachlorobiphenyl
27-4	53	Tetrachlorobiphenyl	75-4	52	Tetrachlorobiphenyl
	65	Tetrachlorobiphenyl		79	Pentachlorobiphenyl
	118	Tetrachlorobiphenyl		101	Pentachlorobiphenyl
27-5	30	Trichlorobiphenyl	75-5	28	Trichlorobiphenyl
	50	Trichlorobiphenyl		37	Trichlorobiphenyl
	56	Tetrachlorobiphenyl		46	Trichlorobiphenyl
	99	Tetrachlorobiphenyl		73	Tetrachlorobiphenyl
	108	Tetrachlorobiphenyl		99	Tetrachlorobiphenyl
	148	Pentachlorobiphenyl		119	DDE
				136	Pentachlorobiphenyl
				219	Pentachlorobiphenyl
27-6	54	Trichlorobiphenyl	75-6	29	Trichlorobiphenyl
	78	Tetrachlorobiphenyl		35	Trichlorobiphenyl
				53	Trichlorobiphenyl
				73	Tetrachlorobiphenyl
				160	Pentachlorobiphenyl
27-7	31	Trichlorobiphenyl	75-7	83	Tetrachlorobiphenyl
	39	Trichlorobiphenyl			
	86	Tetrachlorobiphenyl			

[1] Twelve fish from Tappan Zee site, 27 miles from the Hudson River mouth.

[2] Thirteen fish from Poughkeepsie site, 75 miles from the Hudson River mouth.

Acknowledgments

The authors wish to thank the following persons from the New York State Department of Health, Division of Laboratories and Research: Maria Mahar and Mary Ellen Murphy for technical assistance on this project and Paul Turner for computer assistance.

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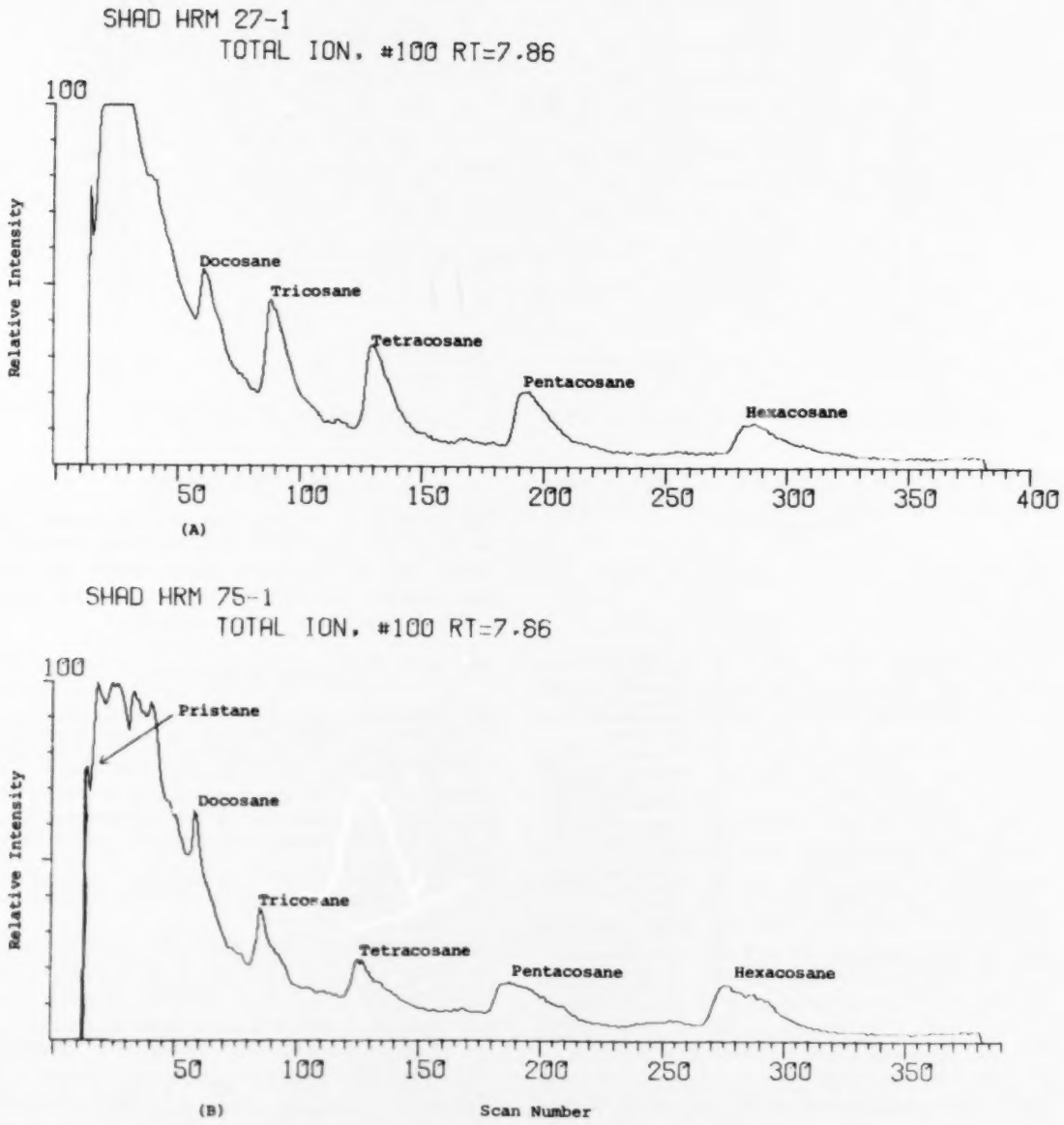

FIGURE 9. *MS total ion chromatograms for (a) Fraction No. 27-1 and (b) Fraction No. 75-1.*

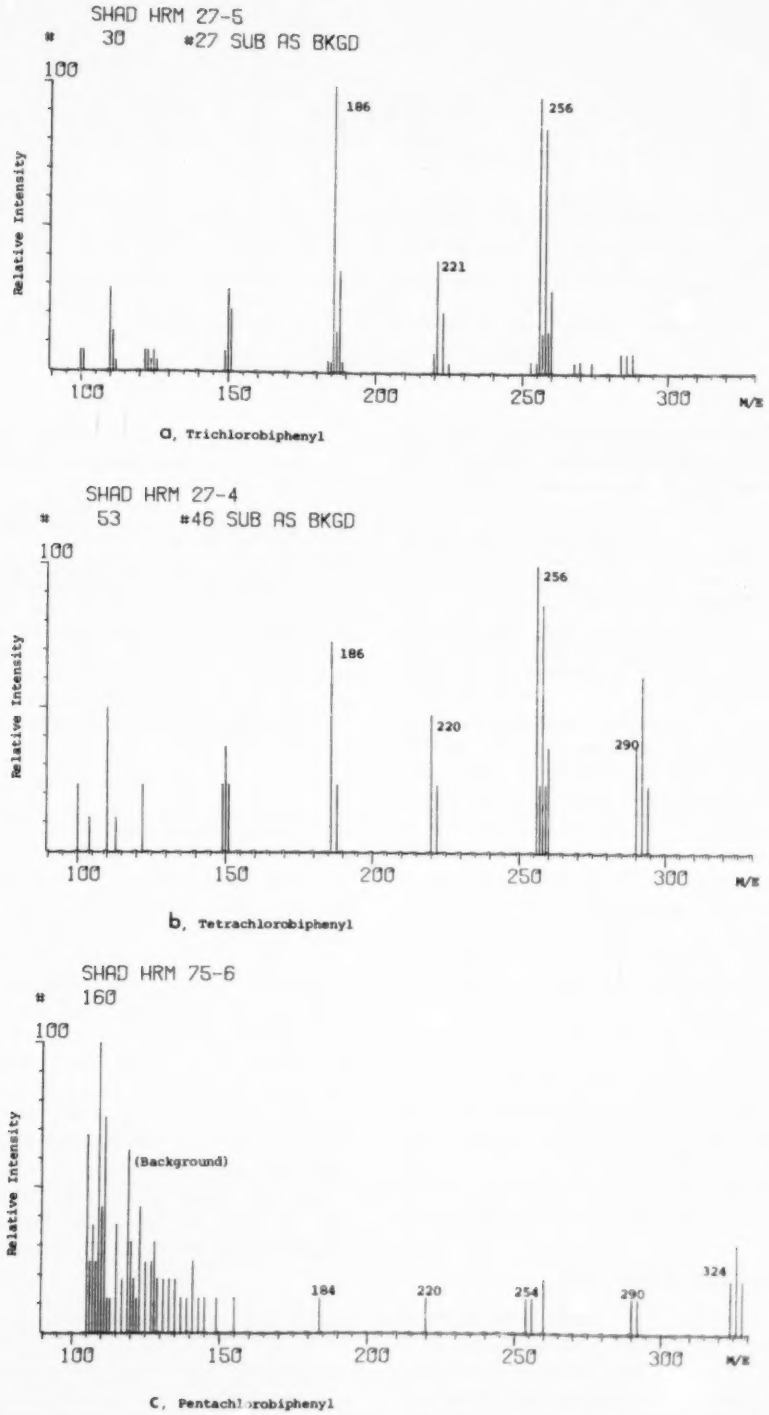

FIGURE 10. *Mass spectra of (a) trichlorobiphenyl, (b) tri- and tetrachlorobiphenyls, and (c) pentachlorobiphenyl.*

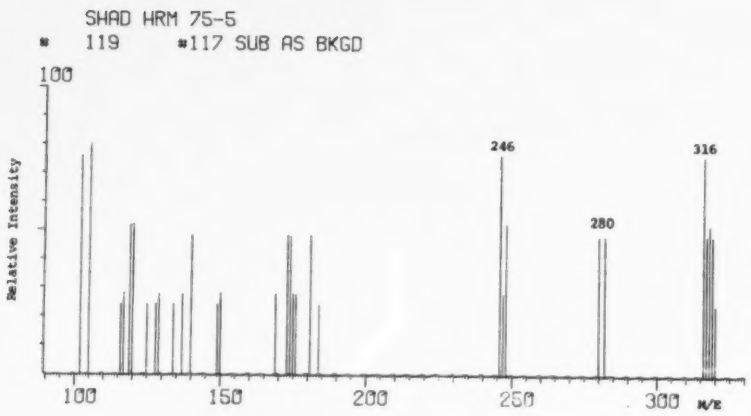

FIGURE 11. *Mass spectrum of DDE.*

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SOILS

Residual Concentrations of Propanil, TCAB, and Other Pesticides in Rice-Growing Soils in the United States, 1972

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ABSTRACT

Ninety-nine soil samples from the rice-growing states of Arkansas, California, Louisiana, Mississippi, and Texas were collected, primarily to monitor the herbicide propanil. No residual concentrations of propanil were detected in any of these samples, but TCAB, a propanil transformation product, was detected in six samples at concentrations ranging from 0.01 ppm to 0.05 ppm. Organochlorine and organphosphorus pesticide determinations were also performed. The compounds dieldrin, aldrin, and DDT and its metabolites were found more frequently; endrin and chlordane were found less frequently. The organophosphorus pesticides diazinon and parathion were detected occasionally.

Introduction

Since 1961, propanil (3′,4′-dichloropropionanilide) has been used as a selective, post-emergence herbicide in the major, rice-growing areas of the United States. In the past few years, propanil has been studied because some of its transformation products have chemical structures similar to those of carcinogens (*1, 2, 4, 5, 15*). The formation of azobenzene compounds in soils where aniline-based herbicides have been applied has been documented (*5, 9*). The formation of these compounds from propanil has also been shown to be affected by other pesticides (*10*), by the nutrient status of the soil (*13*), and by physical conditions (*3*). Most of these data have been determined through laboratory studies, but the formation of these azobenzenes has also been documented in limited field studies (*12*). The major objective of the present study was to determine the concentrations of propanil, TCAB (3.3′,4.4′-tetrachloroazobenzene, a transformation product of propanil), and other selected organochlorine and organophosphorus pesticides in soil and rice under actual use conditions. All of the soil analyses were completed and only those results are reported here.

Sampling Procedures

Soil samples were collected during late summer 1972 from 99 sites located in Arkansas, California, Louisiana, Mississippi, and Texas. The number of sampling sites within states and counties was proportional to the amount of land used for rice production in those areas. Each site represents approximately 6,073 hectares (15,000 acres). When more than one site was allocated to a county, the county was divided into quadrants, and the required number of sites were randomly selected from among the quandrants. Field personnel were instructed to select fields for sampling where propanil had been applied. Information on the kinds and amounts of pesticides applied to the sampling sites was obtained in a personal interview with the landowner or operator.

Each sampling site was 231 square meters, usually a 15.2 meter by 15.2 meter plot, from which 16 soil cores (5.1 cm in diameter by 7.6 cm deep) were collected on an evenly spaced, 4 x 4 grid. A detailed description of the sampling technique has been reported previously (*9*). The 16 cores were composited, sifted through a 6.3-mm sieve, and shipped to the Toxicant Analysis Center, Bay St. Louis, Mississippi, for analysis.

Analytical Procedures

PROPANIL AND TCAB

From the thoroughly mixed field sample, a 100-g subsample was weighed into a 500-ml Erlenmeyer flask. The sample was extracted by shaking with 200 ml of a 1:1 mixture of acetone:benzene for 2 hr on a reciprocating shaker. The supernatant liquid was decanted into

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a 500-ml separatory funnel and washed three times with 100-ml portions of distilled water to remove the acetone. The benzene extract was dried with anhydrous sodium sulfate and concentrated 10:1 for determination of propanil and TCAB.

Determinations were performed on gas chromatographs equipped with tritium foil electron-affinity detectors. Instrument parameters and operating conditions were as follows:

Gas chromatographs:	Micro Tek 220	
Columns:	Glass, 183 cm long, 6 mm OD by 4 mm ID, packed with one of the following: 3 percent DC-200 on 100–120-mesh Gas-Chrom Q; a mixture of 1.5 percent OV-17 and 1.95 percent OV-210 on 100–120-mesh Supelcoport; or 10 percent DC-200 on 100–120-mesh Gas-Chrom Q	
Temperatures, °C:	detector	200
	injection port	250
	DC-200 columns	195
	mixed column	195
Carrier gases:	5 percent methane in argon flowing at 80 ml/minute	

Propanil and TCAB were identified on the 3 percent DC-200 column with an electron-capture detector. Minimum detectable levels of residues were 0.005 ppm propanil and 0.20 ppb TCAB. Identity was confirmed on the 3 percent mixed column by EC detector; minimum detectable levels were comparable to those on the DC-200 column. Additional confirmation was accomplished with a Dohrmann microcoulometric detector in the halogen mode, on a 10 percent DC-200 column. Minimum detectable levels with the microcoulometric detector were 0.025 ppm propanil and 0.02 ppm TCAB. Recovery averaged 90 percent for propanil and 86 percent for TCAB. All concentrations reported in the tables were corrected for recovery, and were converted to a dry weight basis.

ORGANOCHLORINE AND ORGANOPHOSPHORUS PESTICIDES

The analytical method for determining organochlorine and organophosphorus pesticides has been described previously (*10*). Minimum detectable levels for organochlorines and trifluralin were 0.002–0.03 ppm except for combinations of polychlorinated biphenyls (PCBs), chlordane, toxaphene, and other compounds which had minimum detectable levels of 0.05–0.1 ppm. Minimum detectable levels for organophosphates were 0.01–0.03 ppm. Average recoveries by this procedure were 93 percent for organochlorines and 85 percent for organophosphates. All concentrations reported in the tables were corrected for recovery and were converted to a dry weight basis.

Results and Discussion

Of the 99 sites sampled, 81 sites or 82 percent received applications of propanil ranging from 1.2 kg/ha to 11.2 kg/ha (1.1–10.0 lb/acre) during the sampling year. Ten of the 81 sites had received applications of propanil over a four-year period prior to sampling, seven sites were known to have had no propanil applications, and the pesticide use history was unknown for 11 sites.

The results obtained for propanil and TCAB are presented in Table 1. No residue of propanil was detected in any of the 99 soil samples analyzed, but six of the 99 samples (6.1 percent) contained TCAB. TCAB concentrations ranged from 0.01 ppm to 0.05 ppm. These results indicate that the frequency of occurrence and residue concentrations of TCAB are probably quite low.

The results of analyses of soil samples for organochlorine and organophosphorus pesticides are shown in Table 2. Dieldrin, aldrin, and DDT and its metabolites were found most frequently; endrin and chlordane, less frequently. The organophosphorus pesticides diazinon and parathion were detected occasionally. Polychlorinated biphenyls (PCBs) were detected in one soil sample from Arkansas.

The occurrence of organochlorine residues in the rice-growing region is generally similar to that reported by other residue monitoring studies conducted in the same region (*7, 8*).

TABLE 1. *Concentrations of propanil and ACTB in soils from rice-growing areas of the United States, 1972*

State	No. of Samples	% Positive Samples		Residues, ppm Dry wt			
		Propanil	TCAB	TCAB Arithmetic Mean	TCAB Positive Arithmetic Mean [1]	Detected Values Min.	Max.
Arkansas	24	ND	12.5	0.01	0.01	0.01	
California	19	ND	5.3	0.01	0.01	0.01	
Louisiana	28	ND	7.1	0.01	0.03	0.01	0.05
Mississippi	3	ND	ND	—	—		
Texas	25	ND	ND	—	—		
All states	99	ND	6.1	0.01	0.02	0.01	0.05

NOTE: ND = Not detected.
[1] Positive arithmetic mean = Sum of concentrations of positive samples/number of positive samples.

TABLE 2. *Concentrations of organochlorine and organophosphorus compounds in soils from rice-growing areas of the United States, 1972*

State	No. of Samples	Residues, ppm Dry wt											
		Dieldrin	Aldrin	Endrin	Chlordane	Diazinon	Parathion	PCBs	p,p'-DDT	o,p'-DDT	p,p'-DDE	p,p'-TDE	ΣDDT
Arkansas	24												
Range of detected residues [1]		0.01–0.27	0.01–0.25	ND	ND	ND	0.12	1.13	0.01–0.09	0.02	0.01–0.57	0.01–0.21	0.01–0.57
Arithmetic mean		0.08	0.03	—	—	—	0.01	0.05	0.02	<0.01	0.05	0.03	0.09
% Positive samples		95.8	62.5	—	—	—	4.2	4.2	37.5	4.1	33.3	41.7	54.1
California	19												
Range of detected residues		0.01–0.06	0.01	0.17	ND	ND	0.01	ND	0.01–0.25	ND	0.01–0.15	0.01–0.39	0.01–0.39
Arithmetic mean		0.01	<0.01	<0.01	—	—	<0.01	—	0.02	—	0.05	0.01	0.17
% Positive samples		52.6	5.3	5.3	—	—	10.5	—	52.6	—	89.5	89.5	89.4
Louisiana	28												
Range of detected residues		0.01–0.16	0.01–0.07	ND	0.01–0.27	ND	ND	ND	0.02–0.44	ND	0.02–0.25	0.08–0.94	0.02–0.94
Arithmetic mean		0.04	<0.01	—	0.01	—	—	—	0.02	—	0.01	0.04	0.06
% Positive samples		89.3	25.0	—	7.1	—	—	—	10.7	—	7.1	7.1	7.1
Texas	25												
Range of detected residues		0.01–0.10	0.02–0.12	ND	0.02–0.21	0.01–0.06	ND	ND	0.03–0.06	ND	0.01	0.02	0.01–0.06
Arithmetic mean		0.03	0.02	—	0.06	0.01	—	—	<0.01	—	<0.01	<0.01	<0.01
% Positive samples		92.0	56.0	—	76.0	28.0	—	—	8.0	—	4.0	4.0	12.0
Mississippi	3												
Range of detected residues		0.01–0.09	0.05	ND	ND	ND	ND	ND	0.06–0.07	ND	0.02–0.08	0.02–0.08	0.02–0.08
Arithmetic mean		0.04	0.02	—	—	—	—	—	0.04	—	0.04	0.04	0.13
% Positive samples		100.0	33.3	—	—	—	—	—	66.7	—	100.0	100.0	100.0
All states	99												
Range of detected residues		0.01–0.27	0.01–0.25	0.17	0.01–0.27	0.01–0.06	0.01–0.12	1.13	0.01–0.04	0.02	0.01–0.57	0.01–0.94	0.01–0.94
Arithmetic mean		0.04	0.01	<0.01	0.02	<0.01	<0.01	0.01	0.02	<0.01	0.02	0.05	0.08
% Positive samples		84.8	39.4	1.1	21.2	7.8	3.3	1.1	25.3	1.1	31.3	33.3	38.4

NOTE: ND = none detected.
[1] Range does not include zero values.

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Polychlorinated Biphenyl Contamination of Areas Surrounding Two Transformer Salvage Companies, Colman, South Dakota—September 1977 [1]

Yvonne A. Greichus [2] and Barbara A. Dohman [3]

ABSTRACT

Soil, corn plants, and foliage from areas surrounding two electrical salvage companies involved in reconditioning old transformers had unusually high levels of polychlorinated biphenyls (PCBs). Levels decreased as distance from the factories increased. PCBs were dispersed into the air through incineration of waste oils; water and soil contamination was caused by runoff from the factories. PCBs found in the contaminated areas closely resembled Aroclor 1260 as did the PCBs in the waste oil, whereas PCBs in other areas were more similar to Aroclor 1254. PCBs on surface soils taken from an unplowed pasture near the factories also resembled Aroclor 1260, whereas samples taken from depths of 2–4 inches showed degradation of some PCB isomers. PCB concentrations in corn cobs and kernels were < 0.05 ppm, whereas leaves contained PCB levels of up to 2.2 ppm. PCB levels in earthworms and small rodents collected near the factories were considerably higher than levels in the same types of animals collected from other areas.

Introduction

Polychlorinated biphenyls (PCBs) have become significant environmental pollutants which are residual and toxic. Their accumulation in the food chains of many animals produces both acute and chronic effects on reproduction, growth, and behavior (*3, 6, 8*). PCBs have been used extensively in the past as a dielectric base for transformers and capacitors. Although PCBs are no longer manufactured in the United States, the U.S. Environmental Protection Agency (EPA) has estimated that, since their introduction in 1929, 1.25 billion pounds have been used. Of this amount, 60 percent is still in use and 4.4 percent has been destroyed. The rest remains in the environment (*9*). Movement of PCBs through the atmosphere has been demonstrated, and industrial or metropolitan areas are the suspected sources of the PCB contamination (*4, 7*). Ballschmiter et al. (*1*) have shown that certain isomers of PCBs occurred in the environment in the same ratios as measured in commercial PCB mixtures: Aroclors 1254 and 1260. They have presented evidence that the degradation of these isomers in the ecosphere, over 20–40 years, has been too small to produce observable changes, indicating that these isomers are extremely persistant. To further complicate matters, PCBs contain some highly toxic polychlorinated dibenzofurans (*10*). Aroclor 1254 and Aroclor 1260 contain 5.6 ppm and 2.2 ppm, respectively, of a combination of the tetra-, penta-, and hexachlorinated dibenzofurans (*5*).

When the environment has been found to be contaminated with PCBs, several important questions must be considered. If possible, the source of the contamination should be located; the method of dispersion into the environment by air, water, soil, etc., needs to be examined; and the extent of the area of pollution must be determined. Whether the contamination is of recent and/or past origin, the potential harm to the environment due to accumulation in the food chain of animals should be studied. This paper discusses an incident in which PCBs entered the environment through activities of two transformer salvage companies, and it presents methods and supporting data for answering the above questions.

Methods and Materials

During September 1977, two samples each of soil and corn leaves collected near two electrical salvage companies near Colman, South Dakota, were found to have unusually high levels of PCBs. Samples were collected in chemically cleaned glass jars or hexane-washed aluminum foil and were frozen until being analyzed. The samples were extracted and subjected to Florisil column cleanup according to the method of Greichus et al. (*2*). Instrument parameters and operating conditions for gas chromatographic analysis were as follows:

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[1] This paper is published with the approval of the Director of the South Dakota Agricultural Experiment Station as Journal Series Publication No. 1645.

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Gas chromatograph:	Varian Aerograph Model 2100
Detectors:	^{63}Ni and Sc-^{3}H electron-capture
Recorders:	Beckman 10-inch, 1 mv
Columns:	6-ft by ⅛-inch borosilicate glass, packed with 15 percent QF-1 silicone (Fluoro) or a 1:1 mixture of 15 percent QF-1 and 10 percent DC-200 silicone, both on 60–100-mesh Chromosorb W (HP), acid-washed and dimethylchlorosilane-treated
Carrier gas:	nitrogen flowing at 40 ml/minute
Temperatures:	column 210°C injector 220°C detector 290°C ^{63}Ni, or 250°C Sc-^{3}H

Mean recovery of PCBs from fortified samples were 90 percent ± 5 percent standard deviation for all types of samples analyzed. Residue values were corrected for percent recovery. The earlier findings of PCBs in soil and corn leaves prompted the collection of soil, corn leaves, and foliage samples up to 0.25 mile north, 2.5 miles west, and 10 miles south of the factories. Winds in that area are predominantly northwesterly in the fall and winter and southerly in the summer. The town of Colman lies to the east of the factories, and this area was not sampled.

Results and Discussion

Levels of PCBs as Aroclor 1260 on a ppm dry weight basis for the samples collected are shown in Figure 1. Highest PCB levels were found in the samples collected nearest to the factories; PCB levels became progressively lower as distance from the factories increased. An exception was soil samples taken from a drainage ditch to the west of the factory lot where levels reached 46 ppm in a low lying area.

Numerous soil, corn leaf, and foliage samples taken over a number of years from relatively noncontaminated areas of South Dakota have revealed a background level

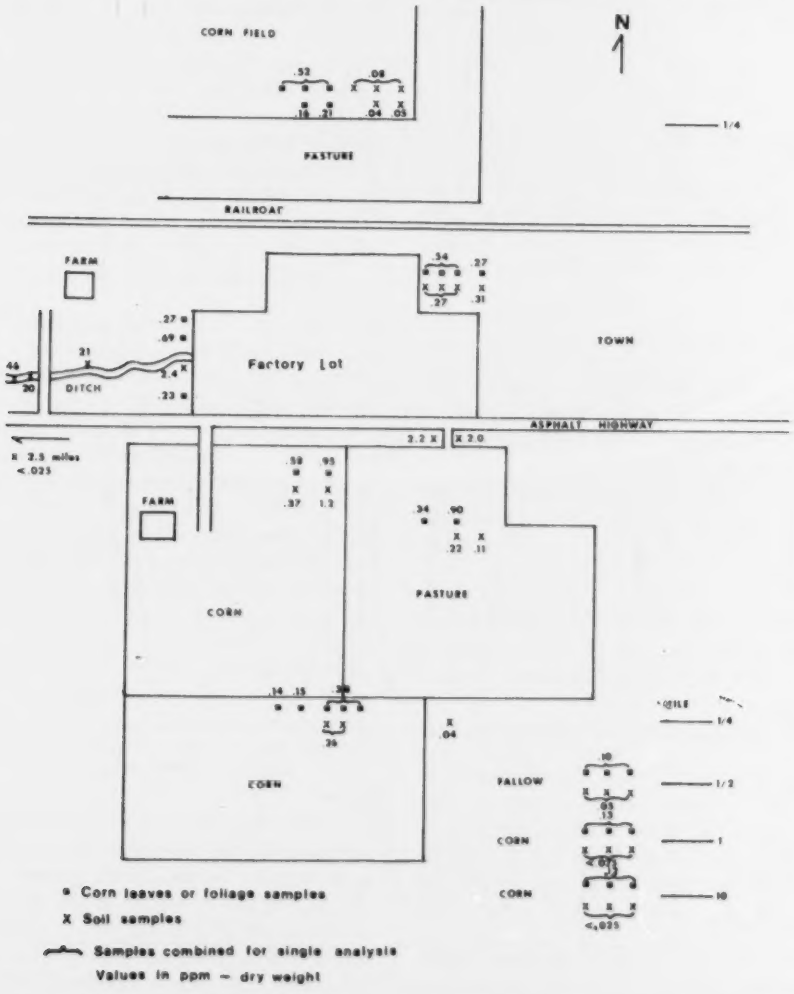

FIGURE 1. *Area surrounding Colman, South Dakota: factory lot consists of two companies adjacent to each other. ppm PCBs as Aroclor 1260.*

of < 0.1 ppm PCBs as Aroclor 1254. Therefore, the PCB levels were above expected concentrations at distances from the factories at least 0.25 mile north, less than 2.5 miles west (soil), and up to 10 miles south (corn leaves) (Fig. 1). One mile south of the factories, the soil contained < 0.025 ppm PCBs, the expected background level, although at 10 miles south of the factories, corn leaves contained 0.12 ppm PCBs, whereas the PCB levels in soil were still < 0.025 ppm, indicating airborne contamination of the leaves. This conclusion was further supported by the analysis of two entire corn plants and the soil on their roots taken 50 yards south of the factory lot (Table 1). The outer leaves contained 1.1 ppm and 2.2 ppm PCBs, the inner leaves contained 0.25 ppm and 0.34 ppm, and the kernels and cobs contained < 0.05 ppm. The 0.29 ppm and 0.53 ppm PCB levels in the roots were somewhat higher than levels in the soil on the roots, but the low levels in the stocks, cobs, and kernels did not indicate significant transport of the PCBs from the roots to the outer leaves. PCBs in the soil could be due to water drainage from one of the factories as well as from air and dust-borne material, since there was drainage from one factory into this area.

PCBs in surface soils and in corn leaves closely resembled commercial Aroclor 1260 as shown by gas chromatograms in Figure 2. The type of PCB found in waste oils (42 ppm) from one factory also resembled Aroclor 1260 (personal communication, U.S. EPA, Denver, Colo.), whereas PCBs in soils and bottom sediments

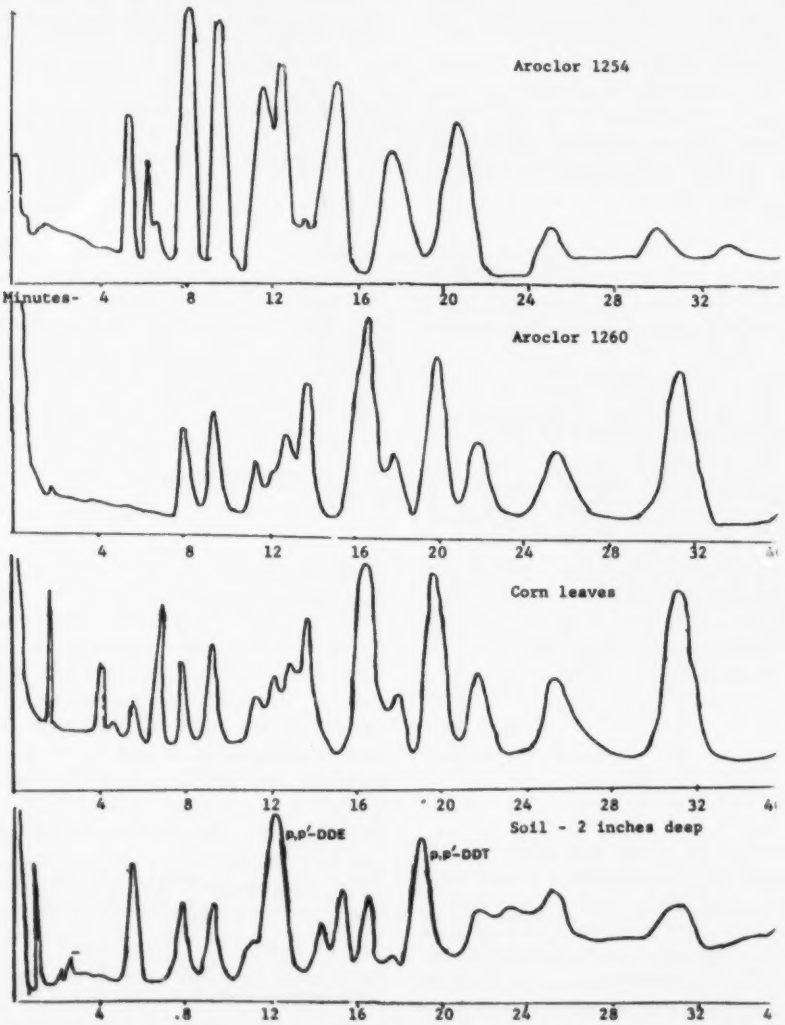

FIGURE 2. *Chromatograms of samples compared to standards of Aroclor 1254 and 1260. See text for instrument parameters and operating conditions.*

TABLE 1. *PCB levels (as Aroclor 1260) in corn plants and soil on roots, 50 yards south of the factory lot, Colman, South Dakota—September 1977*

Sample Type	PCBs, ppm Dry Wt	
	Sample No. 1	Sample No. 2
Soil on roots	0.22	0.24
Roots	0.29	0.53
Stock		
Bottom	0.12	<0.1
Middle	0.14	<0.1
Top	0.23	<0.1
Cob	<0.05	<0.05
Kernels	<0.05	<0.05
Inner leaves on ear	0.25	0.34
Leaves on plant	1.1	2.2

NOTE: Samples 1 and 2 each consists of one entire corn plant approximately 10 feet apart.

from other areas in South Dakota did not. Soil taken at 2–4-inch depths from a pasture across the road from one factory, which had not been plowed since 1960, averaged 0.16 ppm PCBs. In the past, both factories had disposed of surplus transformer oil by incineration, and one factory used waste oil to heat the office building and the shop area (personal communication, U.S. EPA, Denver, Colo.). About four years ago, special furnaces were equipped with afterburners to destroy the PCBs. However, the presence of high levels of PCBs on the corn leaves suggests afterburners may not be efficient.

Samples taken from around one factory and analyzed by the U.S. EPA Laboratory in Denver, Colorado, contained PCBs resembling Aroclor 1260 in the following amounts: water collected from the area behind one shop building, 19 ppb; dirt from in front of an incinerator, 31 ppm; and swabs from three windows on a building next to the incinerator, 14 μg/area. There was no contamination of the Colman drinking water. Soil and vegetation taken one mile north of the factories contained 0.011 ppm PCBs. Sediment and vegetation collected about 20 ft west of a fence around one factory contained 0.17 ppm and 0.39 ppm PCBs, respectively. Soil and corn foliage taken 1 mile west of the factories, from the north side of the highway, contained < 0.02 ppm PCBs. No PCBs were detected on corn, cornstalks, and leaves taken about 1 mile east of the factories (personal communication, Food and Drug Administration, Denver, Colo.).

Earthworms and small rodents were collected from the north and south of the factories and from areas near Brookings, South Dakota, believed to be relatively free of PCBs. Earthworms near the factories and near Brookings contained average PCB levels of 1.96 ppm and 0.77 ppm, respectively, with a ratio of levels in the factory area to levels in the Brookings area of 2.5 (Table 2). PCB levels in rodents near the factories ranged from 4.85 to 17.2 ppm in liver tissues and from 3.42 to 6.87 ppm in muscle tissues. PCB levels in rodents collected near Brookings ranged from 2.20 to 4.67 ppm in liver tissues and from 1.72 to 2.60 ppm in muscle tissues.

TABLE 2. *PCB levels in earthworms and rodents collected near Colman factories and in the Brookings, South Dakota, vicinity, September 1977*

Description	PCBs, ppm		
	Factory Area	Brookings Area	Ratio of Factory/ Brookings
Earthworms[1]	1.85	0.84	2.5
(*Oligochaeta terrestrial*)	2.07	0.67	
		0.54	
Vole (*Microtus* sp.)			
Liver	9.17	4.67	1.5
	4.85		
Muscle	5.68	2.60	1.7
	3.42		
Field mouse (*Peromuscus* sp.)			
Liver	9.52	2.95	4.7
	9.10	2.20	
	17.2		
Muscle	3.77	1.80	3.1
	6.87	1.72	
	5.91		
13-Lined ground squirrel (*Spermophilus* sp.)			
Liver	8.71	0.41	8.4
		1.28	
		1.44	
Muscle	2.89	0.72	3.2
		1.11	
		0.86	

[1] Each sample consisted of 2.6 g dry weight of worms.

Conclusions

The sources of the PCBs in the Colman area were related to operations involved in electrical salvage as evidenced by the predominance of Aroclor 1260 in the factory oil and in surrounding areas and by the fact that the highest levels were near the factories and became increasingly lower as the distance from the factories increased.

PCBs were dispersed by wind, water, and silt runoff in the immediate area. More distant PCB contamination was primarily airborne because PCB levels in outer corn leaves were unexpectedly high whereas soil levels were very low. Airborne contamination extended at least 0.25 mile north and 10 miles south of the factories.

The contamination was of both past and of recent origins. Levels of PCBs (Aroclor 1260) on outer corn leaves proved recent origin, and PCB levels in soil samples taken 2–4 inches deep from a pasture which had not been plowed since 1960 suggested past contamination.

Bioaccumulation is occurring because PCB levels in earthworms and small rodents collected near the factories were considerably higher than levels in the same types of animals collected from other areas.

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APPENDIX

Chemical Names of Compounds Discussed in This Issue

ACEPHATE	*O,S*-Dimethyl acetylphosphoramidothioate
ALDRIN	Hexachlorohexahydro-*endo,exo*-dimethanonaphthalene 95% and related compounds 5%
AROCLOR 1016 or 1242	PCB, approximately 42% chlorine
AROCLOR 1221	PCB, approximately 21% chlorine
AROCLOR 1232	PCB, approximately 32% chlorine
AROCLOR 1248	PCB, approximately 48% chlorine
AROCLOR 1254	PCB, approximately 54% chlorine
AROCLOR 1260	PCB, approximately 60% chlorine
BHC (Benzene Hexachloride)	1,2,3,4,5,6-Hexachlorocyclohexane (mixture of isomers)
CHLORDANE	1,2,3,4,5,6,7,8,8-Octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene. The technical product is a mixture of several compounds including heptachlor, chlordene, and two isomeric forms of chlordane.
DBP	Dibutyl phthalate
DDE	Dichlorodiphenyldichloroethylene (degradation product of DDT); *p,p'*-DDE: 1,1-Dichloro-2,2-bis(*p*-chlorophenyl) ethylene; *o,p'*-DDE: 1,1-Dichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl) ethylene
DDT	Main component (*p,p'*-DDT): ά-Bis(*p*-chlorophenyl) β,β,β-trichloroethane. Other isomers are possible and some are present in the commercial product. *o,p'*-DDT: [1,1,1-Trichloro-2-(*o*-chlorophenyl)2-(*p*-chlorophenyl) ethane]
DIAZINON	*O,O*-Diethyl *O*-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate
DIELDRIN	Not less than 85% of 1,2,3,4,10,10-hexachloro-6,7,-epoxy-1,4,4a,5,6,7:8,8a-octahydro-1,4-*endo-exo*-5,8-dimethano-naphthalene
ENDRIN	Hexachloroepoxyoctahydro-*endo,endo*-dimethanonaphthalene
HCB	Hexachlorobenzene
HEPTACHLOR	1,4,5,6,7,8,8-Heptachloro-3a,4,7,7a-tetrahydro-4,7-*endo*-methanoindene
HEPTACHLOR EPOXIDE	1,4,5,6,7,8,8-Heptachloro-2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindan
METHAMIDOPHOS	*O,S*-Dimethyl phosphoramidothioate
MIREX	Dodecachlorooctahydro-1,3,4-metheno-1*H*-cyclobuta[cd]pentalene
NONACHLOR	1,2,3,4,5,6,7,8,8-Nonachlor-3a,4,7,7a-tetrahydro-4,7-methanoindan
OXYCHLORDANE	2,3,4,5,6,6a,7,7-Octachloro-1a,1b,5,5a,6,6a-hexahydro-2,5-methano-2*H*-indeno(1,2-β)oxirene
PARATHION	*O,O*-Diethyl *O*-*p*-nitrophenyl phosphorothioate
PCBs (Polychlorinated Biphenyls)	Mixtures of chlorinated biphenyl compounds having various percentages of chlorine
PROPANIL	3',4'-Dichloropropionanilide
TCAB	3,3',4,4'-Tetrachloroazobenzene
TDE	2,2-Bis(*p*-chlorophenyl)-1,1-dichloroethane (including isomers and dehydrochlorination products)
TOXAPHENE	Chlorinated camphene (67-69% chlorine). Product is a mixture of polychlor bicyclic terpenes with chlorinated camphenes predominating.
TRIFLURALIN	α,α,α-Trifluoro-2,6-dinitro-*N,N*-dipropyl *p*-toluidine

ERRATA

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Page 138: In the paper "Dieldrin and Heptachlor Residues in Dead Gray Bats, Franklin County, Missouri—1976 versus 1977," by D. R. Clark, Jr., R. K. LaVal, and A. J. Krynitsky, the fourth compound listed in Table 1 should be *cis*-Chlordane.

Page 148: In the paper "Organochlorine Pesticide, PCB, and PBB Residues and Necropsy Data for Bald Eagles from 29 States—1975–77," by T. E. Kaiser, W. L. Reichel, L. N. Locke, E. Cromartie, A. J. Krynitsky, T. G. Lamont, B. M. Mulhern, R. M. Prouty, C. J. Stafford, and D. M. Swineford, the second year listed in Table 4 should be 1975; the second line in the right column should read 1975–77, 20 percent (Table 5).

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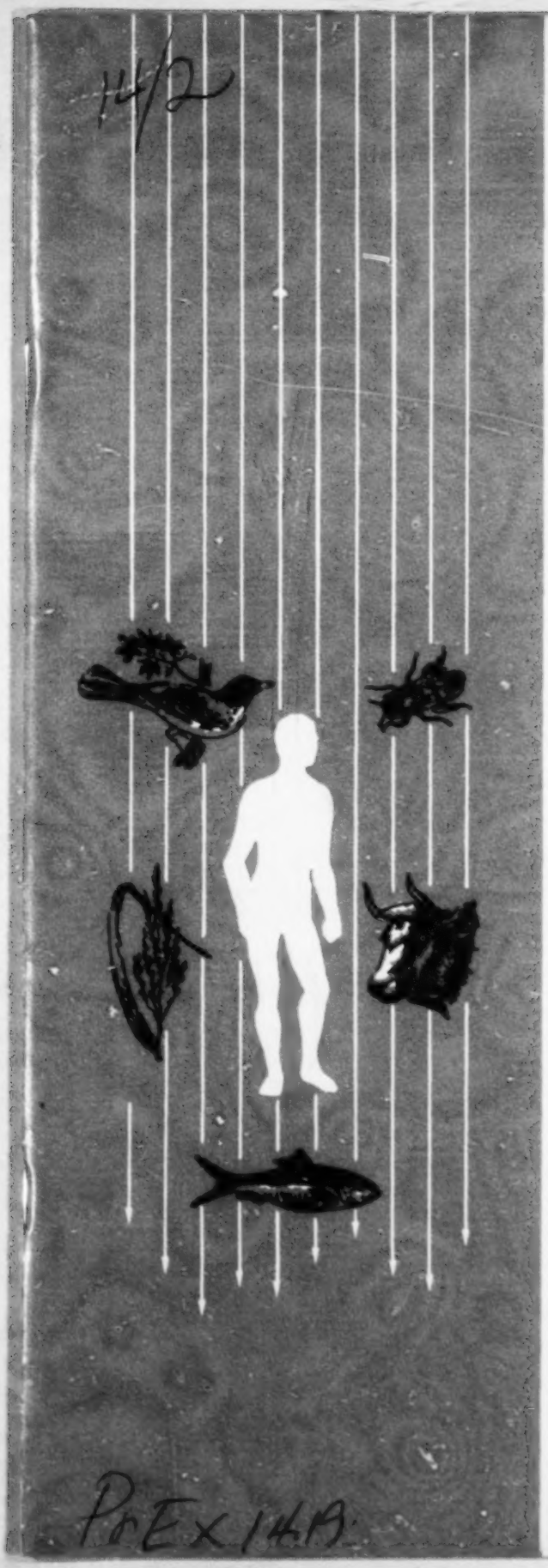

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FISH, WILDLIFE, AND ESTUARIES

Organochlorine Pollutants in Small Cetaceans from the Pacific and South Atlantic Oceans, November 1968–June 1976[1]

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ABSTRACT

Organochlorine residues were analyzed in blubber, brain, or muscle tissues of 69 individuals representing 10 species of small cetaceans. Collections were made from November 1968 through June 1976 at localities in the Eastern Tropical Pacific and along the coasts of California, Hawaii, Japan, and Uruguay. Relations of residue concentrations between tissues are described for DDE and PCBs in two dolphin species. ΣDDT and PCB residues in blubber of most of the 19 individuals of the five southern California species sampled exceed concentrations that are associated with reproductive impairment in pinnipeds, although the nature of such associations is not well defined. The ΣDDT residue of 2,695 ppm in blubber of one California coastal Tursiops truncatus *is one of the highest concentrations reported in tissues of members of any population of wild mammals. Except for one rough-toothed dolphin* (Steno bredanensis) *from Maui, Hawaii, all individuals from all localities surveyed were contaminated with organochlorine compounds. Seventeen different organochlorines were detected; greatest diversity occurred near Japan and California. This is the first report of several of these compounds in tissues of any species of marine mammals. The o,p'-isomers and metabolites of DDT were detected unusually frequently. Ratios of p,p'-DDT to p,p'-DDE in blubber of cetaceans from waters off countries where use of this pesticide has been relatively recent and ongoing were at least an order of magnitude higher than in cetaceans from United States waters.*

Introduction

The status of marine mammal populations is a subject of much recent interest and concern. Legislation, particularly the U.S. Marine Mammal Protection Act of 1972, and international agreements have been formulated with the intention of safeguarding these populations. It is of continuing importance, therefore, to monitor organochlorine pollutants in tissues of these species, many of which occupy high trophic levels in marine food webs.

Elevated concentrations of pesticides and polychlorinated biphenyls (PCBs) are known to occur in blubber of cetaceans (*1, 15, 23*) and pinnipeds (*14, 18*) in geographical areas subject to contamination with these compounds. The present study represents a survey of organochlorine residues in tissues of 69 individuals of 10 species of small cetaceans collected at one South Atlantic and several Pacific localities from November 1968 through June 1976. These localities have had contrasting histories of exposure to organochlorines, and with the exception of two individual specimens from California (*23*), small cetaceans from these areas have not been previously surveyed for residue concentrations. Lack of such information is due partly to the scarcity and difficulty in obtaining adequate specimens suitable for analysis.

Sampling and Analyses

Tissues were obtained from beach-stranded animals or from free-ranging individuals captured by fishermen. All samples from Hawaii, southern California, and Tokyo Bay were taken from beach-stranded animals, except for two pilot whales (*Globicephala macrorhynchus*) which were caught at sea off Los Angeles County, California. Specimens from the remaining localities were takeu at sea. Tissues sampled were blubber, brain, and muscle (*longissimus dorsi*). All dissections were performed by either of the same two investigators, and tissue samples were always taken from the same topo-

[1] Major financial support was provided by U.S. Department of the Interior, Fish and Wildlife Service, through the World Wildlife Fund (U.S. 27); Science and Technology Agency, Tokyo, Japan (STA/PRB/No. 49–438); and the National Science Foundation (GF–42389).

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graphic locations on each specimen. All specimens were preserved in 10 percent formalin. However, due to logistical problems inherent in obtaining tissues from marine mammals, the initial methods of preservation varied with the field situation. Specimens from Uruguay and Japan, except finless porpoises (*Neophocaena phocaenoides*), were immediately preserved in formalin. All California specimens, except two coastal bottlenose dolphins (*Tursiops truncatus*) held frozen for 12 and 18 days and five common dolphins (*Delphinus delphis*) frozen for 1–8 months, were also preserved in formalin on dissection. Other specimens were frozen for various lengths of time before transfer to formalin. Hawaiian dolphins were frozen for 1 month, specimens from the Eastern Tropical Pacific for 2–36 months, and Japanese finless porpoises for 4–57 months. All tissues preserved in formalin were stored in glass jars rinsed with acetone and hexane. Lids were lined with Teflon or aluminum foil. Twenty-five samples of the original preservative stored in similar jars were extracted with hexane and analyzed for organochlorine compounds by gas-liquid chromatography; none was detected.

Collection took place in the western South Atlantic off Uruguay during November–December 1974 and in the Eastern Tropical Pacific between April 1973 and February 1976; all California animals were sampled between May 1974 and June 1976. The Hawaiian strandings occurred in June 1976. Samples from Japan were taken between November 1968 and February 1975. External measurements and notes on stomach contents, parasites, relative age, and reproductive condition were obtained for some of the specimens but are not reported here. These data, as well as precise locations of California stranding sites and specific dates, are available from the authors.

Tissues were removed from formalin and patted dry before being weighed. Residues are expressed as wet weight of preserved tissue. A 10-g portion of homogenized tissue was mixed with anhydrous sodium sulfate and extracted for 7 hours with hexane in a Soxhlet apparatus. An aliquot of the hexane extract, equivalent to a 5-g subsample, 2-g equivalent subsample for blubber, was cleaned on a Florisil column. A portion of the eluate was separated into three fractions on a SilicAR column (*5*). The pesticides in each fraction were identified and quantitated with a gas-liquid chromatograph equipped with an electron-capture detector and a column packed with a mixture of 1.5 percent OV–17 and 1.95 percent QF–1. An OV–275 column was used to confirm and/or quantitate *o,p'*-TDE, *o,p'*-DDT, and *o,p'*-DDE. In some samples where both *o,p'*-DDE and *p,p'*DDE overlapped into fraction III, *cis*-chlordane could not be quantitated. PCBs were estimated by comparing total area of PCB peaks with that of Aroclor 1254 or 1260, depending on which profile the sample more closely resembled. The average recoveries from spiked tissues ranged from 80 percent to 104 percent. Residues were not corrected on the basis of these data.

The lower limit of sensitivity was 0.1 ppm for organochlorines and 0.5 ppm for PCBs. Residues in about 10 percent of the samples were confirmed on a gas chromatograph/mass spectrometer. Residue data are reported by locality, species, sex, tissue, and total body length (an indication of relative age) for each animal. In this way the reader may compute statistics as desired from the original data. Geometric means and 95 percent confidence limits are provided for sample sizes of five or greater. Not-detected values were considered zero in computations; geometric means were therefore calculated on data transformed as $\ln(x + 1)$, with 1 subtracted from the retransformed means.

Results

RESIDUES DETECTED

The principal organochlorine residues detected were PCBs and isomers and metabolites of DDT. Residues of *p,p'*-DDT or its metabolites were detected in all but 1 of the 69 individuals sampled. In addition, *o,p'*-isomers of these compounds, seldom reported in tissue samples of warm-blooded animals from high trophic levels, were also found with unusual frequency (Table 1). One or more of the *o,p'*-isomers were detected in representatives of each species from each locality, except one striped dolphin (*Stenella coeruleoalba*) taken at 7° 0′N, 86° 30′W. Residues of *o,p'*-DDE ranged up to 70 ppm in blubber of common dolphins stranded on southern California beaches. PCBs were also detected in each species at every locality, except for the striped dolphin noted above.

Residues of other organochlorines were present at varying frequencies and concentrations (Table 2). Dieldrin occurred in the blubber of all species except the Fraser's dolphin (*Lagenodelphis hosei*), but not in each species at every locality. Maximum concentrations (up to 38 ppm) were reached in the blubber of finless porpoises from coastal Japan. Hexachlorobenzene (HCB), heptachlor epoxide, and components and metabolites of chlordane also occurred in many samples, but usually at levels below 1.0 ppm (Table 2). Toxaphene was detected in blubber of four species of cetaceans from waters off Japan and in striped dolphins collected at 9° 41′N, 98° 7′W. Endrin, mirex, and *cis*-nonachlor residues (not tabulated) were detected infrequently. Endrin occurred at 0.22 ppm in blubber of a male striped dolphin taken at sea at 9° 41′N, 98° 7′W and at 0.24 ppm in blubber of a male common dolphin stranded in Tokyo Bay. Mirex was found at 0.18 ppm

TABLE 1. *Residues of the principal organochlorine compounds (isomers and metabolites of DDT and PCBs) found in blubber, brain, and muscle tissues of small cetaceans from the Pacific and South Atlantic Oceans, November 1968–June 1976*

Locality and Species	Sex	Tissue (N)	TL	p,p'-DDE	p,p'-TDE	p,p'-DDT	o,p'-DDE	o,p'-TDE	o,p'-DDT	PCBs
URUGUAY										
34°22′S, 53°46′W										
Franciscana dolphin	F	Blubber (3)	116	2.4	2.4	3.0	ND	7.4	0.56	3.6
			133	2.2	1.2	5.6	ND	ND	0.28	4.0
			138	1.9	0.86	4.2	1.7	7.6	7.6	4.2
		Brain (3)	116	ND	ND	ND	ND	ND	ND	0.35
			133	ND	ND	ND	ND	ND	ND	ND
			138	ND	ND	ND	ND	ND	ND	ND
		Muscle (3)	116	ND	ND	ND	ND	ND	ND	0.25
			133	ND	ND	ND	ND	ND	ND	0.13
			138	ND	ND	ND	ND	ND	ND	ND
	M	Blubber (5)	114	5.0	2.8	6.6	0.14	ND	1.4	18
			116	2.6	4.0	10	1.5	11	1.8	3.2
			130	4.4	2.0	7.0	0.10	ND	0.58	5.8
			140	6.4	2.2	7.6	ND	10	1.3	6.8
			145	4.0	1.8	7.2	1.4	4.8	1.1	5.6
			GM	4.3	2.5	7.6	0.50	2.8	1.2	6.8
			CL	2.8–6.4	1.6–3.6	6.2–9.3	ND–1.6	ND–17	0.7–1.8	2.9–14
		Brain (5)	114	ND	ND	ND	ND	ND	ND	ND
			116	ND	ND	ND	ND	ND	ND	ND
			130	ND	ND	ND	ND	ND	ND	0.65
			140	ND	ND	ND	ND	ND	ND	ND
			145	ND	ND	ND	ND	ND	ND	ND
			GM	ND	ND	ND	ND	ND	ND	ND
			CL							0.11
										ND–0.46
		Muscle (5)	CL	ND	ND	ND	ND	ND	ND	ND
EASTERN TROPICAL PACIFIC										
3°26′S, 91°41′W										
Fraser's dolphin	M	Blubber (1)	168	7.2	0.72	1.8	ND	1.3	ND	5.2
		Muscle (1)	168	0.17	ND	ND	ND	ND	ND	ND
4°50′S, 88°12′W										
Striped dolphin	F	Blubber (2)	186	1.6	0.28	0.76	ND	0.74	0.18	ND
			187	4.4	0.26	0.88	ND	ND	ND	ND
		Brain (2)	187	ND	ND	ND	ND	ND	ND	ND
		Muscle (2)	187	ND	ND	ND	ND	ND	ND	ND
	M	Blubber (1)	195	2.8	0.40	1.0	ND	1.0	0.44	5.0
		Brain (1)	195	ND	ND	ND	ND	ND	ND	ND
		Muscle (1)	195	ND	ND	ND	ND	ND	ND	ND
7°0′N, 86°30′W										
Striped dolphin	F	Blubber (1)	192	0.60	ND	0.50	ND	ND	ND	ND
		Muscle (1)	192	ND	ND	ND	ND	ND	ND	ND
7°46′N, 84°20′W										
Striped dolphin	F	Blubber (1)	131	76	4.0	34	ND	1.9	3.0	9.8
		Muscle (1)	131	0.55	0.13	ND	ND	ND	ND	ND
9°41′N, 98°7′W										
Striped dolphin	M	Blubber (2)	148	110	6.0	40	1.1	3.0	13	7.6
			160	120	6.4	40	1.1	3.0	12	6.8
		Muscle (2)	148	1.0	0.25	ND	ND	0.12	ND	ND
			160	1.4	0.25	ND	ND	0.13	ND	ND
		Brain (1)	148	1.1	0.16	ND	ND	ND	ND	0.40
17°53′N, 105°6′W										
Striped dolphin	F	Blubber (1)	180	18	2.0	7.4	ND	1.1	1.6	4.4
		Brain (1)	180	0.2	ND	ND	ND	ND	ND	ND
		Muscle (1)	180	0.19	ND	ND	ND	ND	ND	ND
18°25′N, 110°48′W										
Striped dolphin	F	Blubber (1)	194	22	0.92	3.4	ND	0.44	0.58	5.6
		Brain (1)	194	0.22	ND	ND	ND	ND	ND	ND
		Muscle (1)	194	0.12	ND	ND	ND	ND	ND	ND
20°6′N, 110°29′W										
Striped dolphin	F	Blubber (4)	136	6.6	1.1	2.6	ND	0.66	0.46	1.7
			178	19	1.1	3.8	0.10	0.68	1.5	ND
			188	0.46	ND	0.16	ND	ND	ND	ND
			190	18	1.7	4.2	ND	1.1	0.36	12
		Brain (4)	136	0.12	ND	ND	ND	ND	ND	ND
			178	0.20	ND	ND	ND	ND	ND	ND
			188	ND	ND	ND	ND	ND	ND	ND
			190	0.14	ND	ND	ND	ND	ND	ND

TABLE 1. *Continued*

Locality and Species	Sex	Tissue (N)	TL	*p,p'*-DDE	*p,p'*-TDE	*p,p'*-DDT	*o,p'*-DDE	*o,p'*-TDE	*o,p'*-DDT	PCBs
		Muscle (4)	136	0.11	ND	ND	ND	ND	ND	ND
			178	0.25	ND	ND	ND	ND	ND	ND
			188	ND	ND	ND	ND	ND	ND	ND
			190	0.14	ND	ND	ND	ND	ND	ND
	M	Blubber (1)	208	22	0.68	1.6	ND	0.32	0.52	2.6
		Brain (1)	208	0.30	ND	ND	ND	ND	ND	ND
		Muscle (1)	208	0.38	ND	ND	ND	ND	ND	ND
CALIFORNIA										
32°33'N–35°12'N										
Common dolphin	F	Blubber (3)	182	730	22	21	28	6.8	15	80
			192	360	26	19	26	7.4	12	100
			210	950	51	16	43	8.0	10	160
		Brain (2)	179	20	0.40	0.21	0.39	ND	ND	0.65
			192	14	0.65	ND	0.70	ND	ND	2.2
		Muscle (3)	182	5.5	0.17	ND	0.24	0.12	ND	0.60
			192	4.3	0.28	ND	0.20	ND	ND	0.70
			210	13	0.78	ND	6.8	0.20	ND	3.3
	M	Blubber (10)	184	980	32	26	36	8.8	20	110
			184	780	38	19	40	16	15	160
			187	510	26	18	24	13	9.6	110
			190	1,500	98	36	70	26	42	80
			192	740	44	13	34	22	10	160
			195	780	19	14	23	5.8	14	88
			196	560	24	19	28	8.8	13	110
			198	500	19	15	17	8.0	15	92
			201	1,200	54	22	66	24	28	300
			204	1,700	41	26	29	11	24	140
			GM	847	35	20	34	13	17	123
			CL	620–1,160	24–50	16–25	24–46	8.8–18	12–24	92–163
		Brain (8)	184	20	0.50	ND	0.33	ND	ND	0.70
			187	10	0.24	0.28	0.16	ND	ND	ND
			190	45	1.9	ND	1.0	ND	ND	2.7
			192	17	0.60	ND	0.40	ND	ND	2.0
			195	14	0.21	ND	0.48	0.14	0.13	2.4
			196	11	0.30	ND	0.33	ND	ND	1.2
			201	22	0.60	ND	0.60	ND	ND	1.8
			204	41	0.63	0.19	1.4	0.33	0.28	4.2
			GM	20	0.56	0.05	0.55	0.05	0.05	1.6
			CL	12–31	0.2–1.0	ND–0.2	0.3–0.9	ND–0.33	ND–0.28	0.7–3.0
		Muscle (10)	184	16	0.50	ND	0.63	0.28	ND	2.3
			184	11	0.40	ND	0.15	ND	ND	0.43
			187	5.3	0.22	ND	ND	ND	ND	ND
			190	38	1.9	ND	0.78	ND	ND	2.4
			192	10	0.30	ND	0.25	ND	ND	1.2
			195	7.5	0.21	ND	0.30	0.15	ND	0.78
			196	8.3	0.14	ND	0.19	ND	ND	0.78
			198	16	0.43	ND	0.15	ND	ND	0.70
			201	14	0.43	ND	0.38	ND	ND	1.2
			204	14	0.30	ND	0.48	0.25	ND	1.7
			GM	12	0.43	ND	0.31	0.06	ND	1.0
			CL	8.2–18	0.2–0.7		0.2–0.5	ND–0.2		0.5–1.6
Bottlenose dolphin	F	Blubber (2)	211	1,600	100	46	30	11	9.6	420
			255	2,500	130	54	ND	11	ND	450
		Muscle (2)	211	49	3.7	0.11	1.7	0.53	ND	15
			255	18	0.70	ND	ND	ND	ND	5.5
Pilot whale	F	Blubber (1)	457	30	1.1	1.6	1.6	ND	0.78	8.8
		Muscle (1)	457	0.53	ND	ND	ND	ND	ND	ND
	M	Blubber (1)	670	110	3.4	6.4	4.8	1.1	4.4	14
		Muscle (1)	670	6.5	0.30	0.14	0.24	0.18	0.10	0.88
Harbor porpoise	F	Blubber (1)	140	270	36	11	13	2.2	2.6	84
		Brain (1)	140	2.2	0.15	ND	ND	ND	ND	0.65
		Muscle (1)	140	2.0	0.20	ND	ND	ND	ND	0.50
Dall's porpoise	F	Blubber (1)	183	190	16	14	14	5.2	6.6	94
		Muscle (1)	183	3.8	0.17	ND	ND	ND	ND	0.53
HAWAII										
20°48'N, 156°28'W										
Rough-toothed dolphin	F	Blubber (4)	202	24	0.90	2.2	ND	0.60	1.1	38
			209	15	0.94	1.4	ND	0.86	2.0	26
			215	0.28	ND	ND	ND	ND	ND	ND
			218	ND	ND	ND	ND	ND	ND	ND

TABLE 1. *Continued*

Locality and Species	Sex	Tissue (N)	TL	*p,p'*-DDE	*p,p'*-TDE	*p,p'*-DDT	*o,p'*-DDE	*o,p'*-TDE	*o,p'*-DDT	PCBs
		Brain (1)	218	ND	ND	ND	ND	ND	ND	ND
		Muscle (4)	202	0.21	ND	ND	ND	ND	ND	0.45
			209	0.12	ND	ND	ND	ND	ND	0.14
			215	ND	ND	ND	ND	ND	ND	ND
			218	ND	ND	ND	ND	ND	ND	ND
	M	Blubber (3)	211	7.6	0.62	0.70	ND	0.38	1.2	14
			228	4.2	ND	ND	ND	ND	0.32	7.0
			235	4.6	ND	ND	ND	ND	ND	7.2
		Brain (3)	211	ND	ND	ND	ND	ND	ND	ND
			228	0.78	ND	ND	ND	ND	ND	1.3
			235	0.48	ND	ND	ND	ND	ND	0.78
		Muscle (3)	211	ND	ND	ND	ND	ND	ND	ND
			228	0.22	ND	ND	ND	ND	ND	0.38
			235	0.25	ND	ND	ND	ND	ND	0.33
JAPAN										
34°15′N, 136°52′E										
Striped dolphin	F	Blubber (4)	210	0.64	ND	0.62	ND	ND	ND	1.8
			211	10	1.0	4.6	0.34	1.0	1.1	4.8
			223	8.2	1.4	3.2	0.28	0.55	1.1	4.0
			229	0.88	0.18	0.96	ND	0.14	ND	1.2
		Brain (4)	210	ND	ND	ND	ND	ND	ND	ND
			211	0.23	ND	ND	ND	ND	ND	ND
			223	0.18	ND	ND	ND	ND	ND	ND
			229	ND	ND	ND	ND	ND	ND	ND
		Muscle (4)	210	ND	ND	ND	ND	ND	ND	ND
			211	1.2	0.17	0.38	ND	ND	ND	0.63
			223	0.30	ND	ND	ND	ND	ND	0.85
			229	ND	ND	ND	ND	ND	ND	ND
	M	Blubber (1)	239	12	0.78	4.4	0.30	0.76	0.68	5.0
		Brain (1)	239	0.80	0.16	ND	ND	ND	ND	ND
		Muscle (1)	239	0.63	0.11	ND	ND	ND	ND	1.6
Pilot whale	F	Blubber (5)	332	3.8	0.78	1.6	0.48	0.36	0.24	32
			348	4.4	0.54	2.6	6.62	ND	0.28	6.2
			354	0.56	0.12	0.40	0.14	ND	ND	1.6
			356	1.9	0.32	1.3	0.62	0.12	0.28	0.60
			362	5.2	0.76	2.8	0.58	0.30	0.62	5.8
			GM	2.7	0.48	1.6	0.48	0.15	0.27	4.8
			CL	0.8–6.5	0.2–0.9	0.6–3.2	0.2–0.8	ND–0.4	0.03–0.57	0.4–24
	M	Blubber (1)	355	0.48	ND	0.40	0.12	ND	ND	2.0
34°30′N, 135°E										
Finless porpoise	F	Blubber (3)	118	42	42	26	16	3.4	2.4	88
			163	3.4	2.4	2.8	3.0	0.48	ND	18
			164	20	7.8	6.6	17.0	1.6	1.7	74
		Brain (1)	164	0.15	ND	ND	ND	ND	ND	1.8
		Muscle (2)	164	ND	ND	ND	ND	ND	ND	0.43
			163	0.16	ND	ND	ND	ND	ND	0.70
	M	Blubber (1)	167	62	30	15	15.6	5.8	3.6	96
		Muscle (1)	167	0.45	0.20	ND	ND	ND	ND	1.1
34°30′N, 137°E										
Finless porpoise	F	Blubber (1)	124	14	7.2	7.8	5.6	1.0	1.0	50
		Muscle (1)	124	0.10	ND	0.14	ND	ND	ND	0.63
	M	Blubber (1)	148	32	19	17	10.0	3.4	2.8	64
		Brain (1)	148	0.26	ND	ND	ND	ND	ND	1.3
		Muscle (1)	148	0.35	ND	ND	ND	ND	ND	1.2
35°30′N, 139°50′E										
Common dolphin	F	Blubber (1)	183	0.54	0.46	0.36	0.12	0.34	ND	2.4
		Muscle (1)	183	ND	ND	ND	ND	ND	ND	0.30
	M	Blubber (1)	144	8.2	1.8	4.0	0.40	1.8	0.72	6.4
		Muscle (1)	144	0.28	ND	ND	ND	ND	ND	0.35
43°35′N, 145°55′E										
Dall's porpoise	F	Blubber (1)	184	3.0	1.1	1.4	1.0	1.3	0.78	3.4
		Brain (1)	184	ND	ND	ND	ND	ND	ND	ND
		Muscle (1)	184	ND	ND	ND	ND	ND	ND	0.16

NOTE: (N) = number of individuals sampled; TL = total length of animal in cm; F, M = female, male; ND = not detected; GM = geometric mean; CL = 95% confidence limits.

TABLE 2. *Organochlorine residues other than ΣDDT and PCBs in blubber of small cetaceans from the Pacific and South Atlantic Oceans, November 1968–June 1976*[1]

Locality and Species	Sex (N)	TL	Dieldrin	HCB	Toxaphene	Heptachlor epoxide	*trans*-Nonachlor	Oxychlordane
URUGUAY								
24°22′S, 53°46′W								
Franciscana dolphin	F (3)	116	0.22	0.10	ND	ND	0.12	ND
		133	0.20	ND	ND	ND	ND	ND
		138	0.20	0.10	ND	ND	0.10	ND
	M (5)	114	1.0	ND	ND	ND	0.20	ND
		116	0.52	0.18	ND	ND	0.24	ND
		130	0.38	ND	ND	ND	0.10	ND
		140	0.40	0.12	ND	ND	0.18	ND
		145	0.30	0.10	ND	ND	0.20	ND
		GM	0.50	0.08	ND	ND	0.18	ND
		CL	0.2–0.9	ND–0.2			0.1–0.25	
EASTERN TROPICAL PACIFIC								
3°26′S, 91°41′W								
Fraser's dolphin	M (1)	168	ND	ND	ND	ND	ND	ND
4°50′S, 88°12′W								
Striped dolphin	F (2)	186	0.14	ND	ND	ND	ND	ND
		187	0.14	ND	ND	ND	0.18	ND
	M (1)	195	0.20	ND	ND	ND	ND	ND
7°0′N, 86°30′W								
Striped dolphin	F (1)	192	ND	ND	ND	ND	ND	ND
7°46′N, 84°20′W								
Striped dolphin	F (1)	131	ND	ND	ND	ND	0.22	ND
9°41′N, 98°7′W								
Striped dolphin	M (2)	148	0.84	ND	5.6	0.30	ND	ND
		160	ND	ND	4.0	0.26	ND	ND
17°53′N, 105°6′W								
Striped dolphin	F (1)	180	0.44	ND	ND	ND	0.48	ND
18°25′N, 110°48′W								
Striped dolphin	F (1)	194	ND	ND	ND	ND	ND	ND
20°6′N, 110°29′W								
Striped dolphin	F (4)	136	0.30	ND	ND	ND	0.16	ND
		178	0.40	ND	ND	ND	0.64	ND
		188	ND	ND	ND	ND	ND	ND
		190	0.28	ND	ND	ND	0.24	ND
CALIFORNIA								
32°33′N–35°12′N								
Common dolphin	F (3)	182	ND	0.13	ND	ND	ND	ND
		192	1.1	ND	ND	0.34	ND	0.12
		210	ND	0.24	ND	ND	ND	ND
	M (10)	184	ND	0.18	ND	ND	ND	ND
		184	1.1	0.10	ND	0.30	ND	0.20
		187	ND	0.12	ND	ND	ND	ND
		190	ND	0.34	ND	2.0	ND	1.2
		192	1.4	0.14	ND	ND	10	0.50
		195	ND	0.14	ND	ND	ND	ND
		196	ND	ND	ND	0.12	0.82	0.32
		198	ND	ND	ND	ND	ND	0.20
		201	ND	0.10	ND	0.22	ND	0.20
		204	ND	0.24	ND	ND	ND	ND
		GM	0.18	0.13	ND	0.18	0.35	0.22
		CL	ND–0.5	0.1–0.2		ND–0.5	ND–1.3	0.02–0.5
Bottlenose dolphin	F (2)	211	ND	0.34	ND	0.62	14	3.4
		255	6.4	0.46	ND	ND	21	4.0
Pilot whale	F (1)	457	ND	ND	ND	ND	ND	ND
	M (1)	670	ND	ND	ND	ND	ND	ND
Harbor porpoise	F (1)	140	1.0	0.18	ND	0.18	5.0	ND
Dall's porpoise	F (1)	183	0.40	0.28	ND	ND	0.56	ND

TABLE 2. *Continued*

Locality and Species	Sex (N)	TL	Dieldrin	HCB	Toxaphene	Heptachlor epoxide	*trans*-Nonachlor	Oxychlordane
HAWAII								
20°48′N, 156°28′W								
Rough-toothed dolphin	F (4)	202	0.32	ND	ND	ND	0.64	ND
		209	0.66	ND	ND	ND	1.0	ND
		215	ND	ND	ND	ND	ND	ND
		218	ND	ND	ND	ND	ND	ND
	M (3)	211	0.36	ND	ND	ND	0.50	ND
		228	ND	ND	ND	ND	ND	ND
		235	ND	ND	ND	ND	ND	ND
JAPAN								
34°15′N, 136°52′E								
Striped dolphin	F (4)	210	ND	ND	ND	ND	ND	ND
		211	0.28	0.08	0.18	ND	ND	ND
		223	0.34	ND	ND	ND	0.24	ND
		229	ND	ND	0.12	ND	ND	ND
	M (1)	239	ND	0.10	0.18	ND	0.12	ND
Pilot whale	F (5)	332	ND	ND	0.14	ND	ND	ND
		348	ND	0.06	ND	ND	ND	ND
		354	ND	ND	ND	ND	ND	ND
		356	ND	ND	0.14	ND	ND	ND
		362	1.2	ND	0.14	ND	ND	ND
		GM	0.17	0.01	0.08	ND	ND	ND
		CL	ND–0.8	ND–0.05	ND–0.2			
	M (1)	355	ND	ND	0.12	ND	ND	ND
34°30′N, 135°E								
Finless porpoise	F (3)	118	16	0.64	ND	ND	ND	ND
		163	2	ND	ND	ND	ND	ND
		164	12	0.38	0.22	ND	ND	0.36
	M (1)	167	32	0.42	0.16	0.28	1.1	0.12
34°30′N, 137°E								
Finless porpoise	F (1)	124	16	0.22	ND	0.34	0.40	ND
	M (1)	148	38	0.34	0.14	0.82	ND	0.46
35°30′N, 139°50′E								
Common dolphin	F (1)	183	0.14	0.06	0.14	0.04	ND	ND
	M (1)	144	0.62	0.26	0.36	ND	0.46	ND
43°35′N, 145°55′E								
Dall's porpoise	F (1)	184	0.40	0.28	ND	ND	0.56	ND

NOTE: (N) = number of individuals sampled; TL = total length of animal in cm; F, M = female, male; ND = not detected; GM = geometric mean; CL = 95% confidence limits.

[1] Brain and muscle tissues (sample sizes identical to those in Table 1) had no detectable residues of the compounds listed above except as noted in the text.

in blubber of the male common dolphin from Tokyo Bay and at 0.56 ppm in blubber of a male finless porpoise captured at sea near Himeji, Hyogo Prefecture, Japan. Concentrations of *cis*-nonachlor were 2.2 ppm and 10 ppm in blubber of two beach-stranded southern California female bottlenose dolphins. Residues of *cis*-chlordane were positively identified in blubber of the following cetaceans: two male Franciscana (*Pontoporia blainvillei*) from the western South Atlantic off Uruguay (0.94 ppm and 0.12 ppm); a female striped dolphin collected at 20° 6′N, 110° 29′W (0.18 ppm); a female bottlenose dolphin (13 ppm), a female common dolphin (6.4 ppm), and six male common dolphins (geometric mean 9.8 ppm, range 5.8–36 ppm) from southern California.

RESIDUES BY TISSUES

Blubber has a high lipid content, and organochlorine concentrations are therefore consistently higher in this tissue than in brain or muscle. However, statistical comparisons of residue concentrations within locality, species, and sex are possible only for tissues of male common dolphins from southern California. Mean concentrations of *p,p′*-DDE in blubber, brain, and muscle of these animals (Table 1) differed significantly ($P < 0.01$; two-way analysis of variance on ln + 1 transformed data, mean separation by Student-Newman-Keuls test). Mean PCB concentrations in blubber were significantly greater than those in brain or muscle ($P < 0.01$). Brain and muscle PCB concentrations did not differ ($P > 0.05$). Residue levels of DDE in these three tissues were significantly correlated in common dolphins from southern California and in striped dolphins from the Eastern Tropical Pacific (Table 3). PCB residues in common dolphins showed significant correlation only between brain and muscle (Table 3).

TABLE 3. *Simple linear correlation coefficients (r) between blubber, brain, and muscle tissues containing residues of DDE and PCBs in 13 common dolphins collected at southern California beaches and of DDE in 14 striped dolphins from the Eastern Tropical Pacific, November 1968–June 1976*

Species	Residue		Blubber/ Brain	Blubber/ Muscle	Brain/ Muscle
Common dolphins	DDE	*r*	0.92**	0.65*	0.83**
		DF	7	11	7
	PCB	*r*	−0.04	0.09	0.75**
		DF	7	11	7
Striped dolphins	DDE	*r*	0.99**	0.97**	0.99**
		DF	9	12	9

* $P < 0.05$.
** $P < 0.01$.

PCBs were not detected in muscle and occurred in only one brain sample of Eastern Tropical Pacific striped dolphins.

Except in heavily contaminated individuals, the principal organochlorine compounds found in blubber were not detected in brain or muscle at the same frequencies (Table 1). For example, DDE did not appear in brains of Eastern Tropical Pacific striped dolphins except when blubber residues exceeded about 5–10 ppm (Fig. 1). In contrast, all southern California common dolphins had detectable DDE residues in brains, but blubber residues were 360 ppm or greater (Fig. 1). Similarly, only two of the compounds listed in Table 2 that were found in blubber were also found in brain or muscle. Dieldrin occurred at 0.20 ppm in the muscle of a male finless porpoise collected off Himeji, Japan. Brain or muscle tissues of three common dolphins from southern California beaches contained residues of *trans*-nonachlor. The brain of one female contained 0.25 ppm and those of two males contained 0.33 ppm and 0.23 ppm. Muscle of the two males contained *trans*-nonachlor at 0.16 ppm and 0.12 ppm.

RESIDUES BY LOCALITY

Uruguay—Five male and three female Franciscana were collected offshore from Punta del Diablo, Dept. Rocha (34° 22′S, 53° 46′W). Dieldrin, PCBs, and DDT and its metabolities were present in blubber of all individuals (Tables 1 and 2). Other organochlorines present in blubber included HCB, *trans*-nonachlor, and *cis*-chlordane. PCBs were the only organochlorines detected in muscle and brain. This was the only locality in which residues of *p,p′*-DDT exceeded those of *p,p′*-DDE in blubber (Table 4).

Eastern Tropical Pacific—Striped dolphins were collected at sea at latitudes ranging from 4° 50′S to 20° 6′N (Table 1). In general, striped dolphins from these localities had relatively low to moderate blubber concentrations of PCBs and DDT-related compounds (Table 1). Exceptions included two young males collected at 9° 41′N, 98° 7′W, which contained an

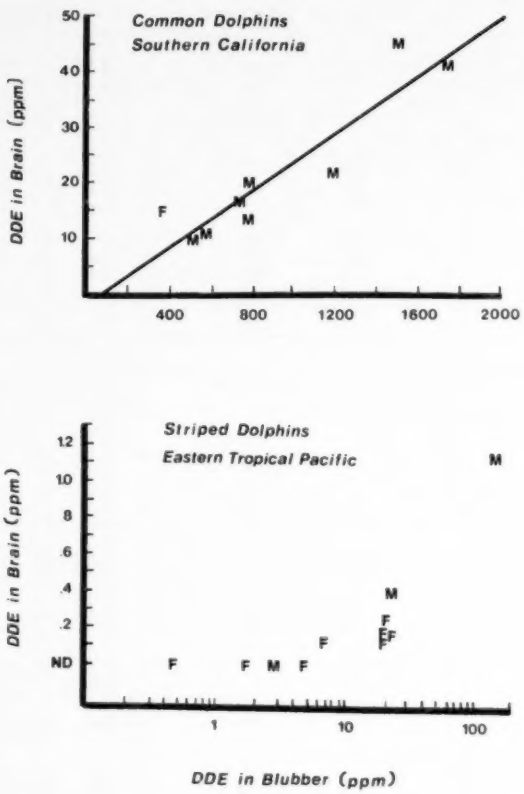

FIGURE 1. *Concentrations of DDE in brains of Southern California common dolphins and Eastern Tropical Pacific striped dolphins in relation to DDE concentrations in blubber (M = male, F = female). Line depicted in top portion of figure is described by equation* $Y = -1.28 + 0.025X$.

average of 115 ppm *p,p′*-DDE in blubber as well as residues of PCBs, dieldrin, and heptachlor epoxide (Tables 1 and 2); toxaphene residues in these specimens were the highest reported in this study. Few compounds other than PCBs and those related to DDT were found in blubber of other striped dolphins. PCBs were not detected in the two females taken at 4° 50′S, 88° 12′W but were found in the male. With the exception of *o,p′*-TDE in muscle tissues of the two males from 9° 41′N, 98° 7′W, brain and muscle tissues of Eastern Tropical Pacific striped dolphins did not possess detectable residues of any organochlorines other than *p,p′*-DDE and *p,p′*-TDE.

The blubber of one male Fraser's dolphin collected at 3° 26′S, 91° 41′W contained residues of PCBs and DDT-related compounds. The predominant compound was *p,p′*-DDE at 7.2 ppm (Table 1).

California—Five species of small cetaceans were sampled on or near southern California beaches at latitudes

TABLE 4. *Ratios of p,p'-DDT to p,p'-DDE in blubber of small cetaceans grouped according to oceanic region or the nearest major land masses at the latitudes of collection, November 1968–June 1976*

Species	Sample Size	$\frac{p,p'\text{-DDT}}{p,p'\text{-DDE}} \pm$ Std Dev
SOUTHERN CALIFORNIA		
Common dolphins	(13)	0.03 ± 0.01
Bottlenose dophins	(2)	0.03 ± 0.004
Pilot whales	(2)	0.06 ± 0.004
Harbor porpoise	(1)	0.04
Dall's porpoise	(1)	0.07
HAWAII		
Rough-toothed dolphins	(6)	0.05 ± 0.05
EASTERN TROPICAL PACIFIC		
Fraser's dolphin	(1)	0.25
Striped dolphins	(14)	0.34 ± 0.18
JAPAN		
Striped dolphins	(5)	0.66 ± 0.35
Pilot whales	(6)	0.63 ± 0.14
Finless porpoise	(6)	0.52 ± 0.21
Common dolphins	(2)	0.58 ± 0.13
Dall's porpoise	(1)	0.47
URUGUAY		
Franciscana	(8)	1.97 ± 0.90

32° 33′N and 35° 12′N. These animals were heavily contaminated with organochlorine residues, including particularly high concentrations of metabolites and isomers of DDT. The inshore-feeding coastal bottlenose dolphins were the most heavily contaminated. Blubber from two immature females stranded in San Diego County in July and August 1976 contained 2,695 and 1,797 ppm ΣDDT, over 400 ppm PCBs, and lesser quantities of dieldrin, heptachlor epoxide, HCB, oxychlordane, *trans*-nonachlor, and *cis*-chlordane (Tables 1 and 2). Blubber of comon dolphins had concentrations of up to 1,831 ppm ΣDDT and 300 ppm PCBs. Up to 48 ppm ΣDDT occurred in brains. With the exception of dieldrin, HCB, and toxaphene, residues of all organochlorines listed in Tables 1 and 2 were higher in these two species in southern California than in any species at any other locality.

High concentrations of organochlorines were also present in the other California specimens. Residues of ΣDDT in blubber reached 335 ppm in an immature female harbor porpoise (*Phocoena phocoena*) stranded in San Luis Obispo County and 246 ppm in an adult female Dall's porpoise (*Phocoenoides dalli*) stranded in San Diego County. Lowest ΣDDT residues in blubber were 35 ppm in an immature female pilot whale incidentally caught off Los Angeles County.

Hawaii—Tissue samples were analyzed from seven rough-toothed dolphins (*Steno bredanensis*) that mass-stranded at Kihei Beach, Maui (20° 58′N, 156° 28′ W). One adult female did not possess detectable residues of organochlorine compounds. This was the sole individual in the entire study that was free of contamination. Isomers and metabolites of DDT were present in blubber of other individuals at relatively low concentrations. PCBs reached 38 ppm in one female. Dieldrin and *trans*-nonachlor were the only additional organochlorines detected at this locality. The blubber of a 93-cm near-term fetus (not tabulated) contained one compound, *p,p'*-DDE, at 0.54 ppm. Maternal blubber also contained only *p,p'*-DDE, at a concentration of 0.28 ppm.

Japan—Striped dolphins and pilot whales were caught by fishermen at Taiji, Wakayama Prefecture (34° 15′N, 136° 52′E), and finless porpoises were taken at Ise Bay (34° 30′N, 137° E) and the Seto Inland Sea (34° 30′N, 135° E). These specimens contained a wide range of organochlorine residues (Tables 1 and 2), including the highest blubber concentrations of dieldrin and HCB found in the study (up to 38 ppm and 0.64 ppm, respectively, in finless porpoises). Toxaphene or toxaphene-like compounds were found in tissues of individuals of all three species and in common dolphins stranded in Tokyo Bay (35° 30′N, 139° 50′E). Toxaphene was detected elsewhere only in striped dolphins taken at 9° 41′N, 98° 7′W. As previously noted, the two common dolphins from Tokyo Bay contained mirex and endrin in addition to the compounds listed in Tables 1 and 2. The highest concentrations of *p,p'*-DDE and PCBs among Japanese cetaceans occurred in finless porpoises, which are also the most highly restricted to inshore feeding. Concentrations of PCBs were higher in blubber of Japanese finless porpoises than in cetaceans from all other localities except southern California. Ratios of *p,p'*-DDT to *p,p'*-DDE were higher in Japanese cetaceans than in those from all other localities except the western South Atlantic off Uruguay (Table 4).

Discussion

Small cetaceans may generally be expected to reflect the extent of local organochlorine contamination in marine ecosystems: they occupy high trophic levels, are large nonmigratory, and are relatively long-lived (*21*). This premise is dramatically supported by residue concentrations in animals from southern California waters. The oceanic input of PCBs from five southern California sewage treatment plants was estimated at nearly 20,000 kg per year in 1972 (*20*), and one Los Angeles area pesticide manufacturer was responsible for a continuous discharge of DDT at sewer outfalls for over 20 years (*19*). Shortly before cessation of this latter practice in 1970, the input of ΣDDT (80 percent of which was DDT) to the ocean from this source alone was estimated to be 250 kg per day (*19*). Cetaceans collected in this region during our study show heavy

contamination with these compounds. With the exception of a single immature female pilot whale taken at sea, blubber from all specimens from beaches or waters off southern California contained residues of *p,p'*-DDE in excess of 100 ppm. Mean concentrations of this compound in blubber of male common dolphins were more than seven times greater than the highest individual values in any species from any other locality in the present study. Maximum residues of *p,p'*-DDE in blubber of two immature female coastal bottlenose dolphins were even higher; *p,p'*-DDE residues were more than twice the highest previously published concentrations of this compound in cetaceans (*23*). PCB residues in blubber of the California *Tursiops* also exceeded previously published concentrations for cetaceans from all parts of the world yet investigated except perhaps the Mediterranean coast of France (*1, 25*). Blubber residues of ΣDDT in one of these females reached 2,695 ppm, a value equivalent to the 2,678 ppm reported in an adult male California sea lion (*Zalophus californianus*) collected near Año Nuevo Island, California (37° 5'N, 122° 20'W), in 1970 (*18*). Concentrations of ΣDDT in California pinnipeds and cetaceans are to the authors' knowledge the highest known for any populations of wild mammals.

Cetaceans from other localities had lower concentrations of the principal organochlorine residues (DDT and PCBs), although these compounds were detected in all species at all localities. The use of DDT on neighboring land masses has presumably had varying histories. Direct discharge of DDT at southern California outfalls took place for over 20 years and had been curtailed for several years before specimen collection (*19*). In addition, the general use of DDT in the United States ended in 1972. Mean ratios of *p,p'*-DDT to *p,p'*-DDE are very low, ranging from 0.03 to 0.07 ppm in all species collected in waters off Hawaii and California (Table 4); long-term accumulation of the persistent metabolite DDE in marine ecosystems, as well as a lack of recent input of DDT, contribute to these low ratios. Mean ratios in cetaceans from other localities (Table 4) are at least an order of magnitude higher, ranging from 0.25 ppm to 0.66 ppm in Eastern Tropical Pacific and Japanese waters to the extreme in Franciscana dolphins from the Western South Atlantic, where residues of DDT exceed those of DDE. (Decomposition of DDT during storage of specimens can also influence these ratios (*7*). However, in comparison to geographic effects, this loss appears to have contributed little to the contrasting values seen in the present study: tissues of California cetaceans, for example, were stored for 23.5 ± 4 months whereas Uruguayan specimens were held 23.9 ± 0.3 months before they were analyzed.) Franciscana are very restricted to coastal waters of this region (*4*; R. L. Brownell, Jr., personal observations), and also extensively use the estuary of the Rio de la Plata. Widespread deforestation and agricultural cultivation are recent phenomena in much of the watershed draining into the Rio de la Plata system, particularly in southeastern Brazil (*17*). In addition, sharp increases in the use of DDT (and loss of fish and wildlife) have recently occurred near Brazil's extensive Lagoa dos Patos (*10*). The entrance to this lagoon is about 250 km north of the Uruguay collection site and the Brazilian Current in this area moves south along the coast. The introduction of DDT into the areas inhabited by Franciscana dolphins thus appears to be relatively recent and ongoing.

Cetaceans from Japanese waters contained a wide array of organochlorine compounds. This is particularly true of finless porpoises, which are the most restricted inshore feeders of all cetaceans surveyed in Japan. Although we know of no accounts documenting the degree of organochlorine contamination in other components of marine ecosystems at these localities, areas such as Ise Bay and the Seto Inland Sea possess some of the most densely industrialized sections of coastline in the world (*22*). This industrialization, along with intensive agricultural practices, apparently correlates with the diversity of organochlorine compounds seen in Japanese cetaceans. Eastern Tropical Pacific striped dolphins usually contained fewer kinds of residues in comparison with Japanese striped dolphins, but concentrations of DDT and PCBs were generally higher. Sources of contamination in these tropical seas are unknown.

In addition to *o,p'*-isomers of DDT and its metabolites, a number of other compounds, which have not been commonly reported in earlier studies, were detected in blubber of cetaceans (Table 2). This is the first report of endrin, toxaphene, *cis*-nonachlor, oxychlordane, or *trans*-nonachlor in tissues of cetaceans. Maximum residues of dieldrin (38 ppm in blubber of Japanese finless porpoises) were more than twice the highest previously reported concentrations (*15*). Residues of *cis*-chlordane in blubber of California common dolphins were nearly three times greater than those in previous reports (*23*). Other than our report of mirex in Japanese cetaceans, the only other marine mammals in which this compound has been detected are harbor seals from the Netherlands (*24*).

Although the present study has shown heavy and widespread contamination of small cetaceans with organochlorine compounds, the impact of this exposure has not yet been determined. Concentrations of ΣDDT and PCBs in blubber lower than those reported here have been associated with impaired reproduction in pinnipeds, but cause-and-effect relationships are not well defined. Population declines and uterine pathology

have been documented in Baltic Sea ringed seals (*Pusa hispida*); nonpregnant females with abnormal uteri had significantly higher mean blubber concentrations of ΣDDT and PCBs (130 ppm and 110 ppm) than pregnant females (88 ppm and 73 ppm) (*13*). On this basis it was concluded that organochlorines were responsible for the observed effects (*13*). However, because loss of organochlorines through lactation and pregnancy is an avenue unavailable to female mammals with imparied reproduction, higher residue concentrations may be expected to occur in non-reproducing females regardless of cause of reproductive failure. Residues in nonpregnant ringed seals with normal uteri, for example, did not differ significantly from those in nonpregnant females exhibiting the pathological changes [$P < 0.05$, *t*-test calculated from data of Helle et al. (*13*)]. A more marked association has been noted between high blubber residues of both ΣDDT (range 626–1039 ppm) and PCBs (85–145 ppm) and premature pupping in California sea lions (*6*). Females producing full-term pups had considerably lower concentrations of these compounds (51–203 ppm ΣDDT, 12–25 ppm PCB) (*6*). Although this relationship appears stronger than that implied by the ringed seal data, it is confounded by additional factors: premature and full-term parturient females differed in age and probably used different feeding areas, and abortion-inducing diseases were present in the population (*8*). It is currently hypothesized that interactions between organochlorines and some of these other factors are responsible for premature pupping (*8*).

Despite the equivocal nature of field observations of associations between high concentrations of organochlorines in blubber and reproduction in pinnipeds, toxic effects of PCBs and DDT or its metabolites, including severe reproductive impairment, have been experimentally verified in other mammals and birds (*3, 11, 12*). Drastic population reductions due to DDE exposure have been well documented in fish-eating birds from marine waters off southern California (*2, 9, 16*). Although the impact of organochlorine pollutants on small cetaceans has not yet been determined, the severe degree of contamination found in cetaceans from these same waters, due largely to what would presently be considered industrial negligence (*19*), should in itself be cause for serious concern.

Acknowledgments

We thank Toshiro Kamiya, Toshio Kasuya, James G. Mead, Nobuyuki Miyazaki, Masaharu Nishiwaki, and Mary Jean Walker for help with the field work. We are grateful to William F. Perrin and Edward Shallenberger for providing some of the specimens. Eugene H. Dustman and Lucille F. Stickel provided critical reviews of the manuscript.

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Use of Selected Freshwater Bivalves for Monitoring Organochlorine Pesticide Residues in Major Mississippi Stream Systems, 1972–73

Richard L. Leard,[1] Billy J. Grantham,[2] and George F. Pessoney[2]

ABSTRACT

Seven species of freshwater Pelecypoda, Amblema costata, Corbicula manilensis, Elliptio crassidens, Lampsilis anadontoides, Lampsilis claibornensis, Megalonaias gigantea, *and* Plectomerus dombeyanus, *were collected and monitored for pesticide content during 1972 and 1973. Thirteen collection sites, representing five major river basins in the state of Mississippi, were sampled and compared. During the 24-month study, 26 water samples and 58 claim samples from the five river basins were analyzed. Individual samples weighed from 8 g to 20 g and consisted of 1–30 clams, depending on size. Residues of toxaphene and methyl parathion were found only in 1973 water samples. The study shows that freshwater clams are effective monitors of pesticide content. The tendency of clams to concentrate pesticides and their corresponding ability to eliminate them varies with species. Significant reductions in DDT and a corresponding buildup of p,p'-TDE were noted in 1973, following the limitations on the use of DDT and large-scale flooding throughout the state.*

Introduction

The tendency of Pelecypoda to accumulate high body levels of pesticides from water containing very small amounts has been demonstrated under laboratory conditions (*2, 5, 7*). In addition, Butler (*2*) and Fikes (*5*) have shown that bivalves are able to eliminate virtually all of their body burden of pesticides when placed in pesticide-free water. Other researchers have investigated pesticide accumulations by marine and freshwater species following periods of spraying or from known pesticides outfalls (*1, 3, 4, 6*).

The present study evaluates the tendency of clams to accumulate pesticides and their ability to eliminate them under field conditions. It was felt that a comparison of 1972 and 1973 samples should reflect purging of high body concentrations as a result of either or both of these factors: the banning in December 1972 of the widespread use of DDT, and the extensive flooding of the state of Mississippi during Spring 1973.

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Sampling

A survey of pesticide levels in selected species of freshwater clams in the major stream systems of the state of Mississippi was conducted in Summer 1972 in order to determine body concentrations of pesticides. All collections were made during periods of low stream flow (July through November). In 1973, clams were again collected from the same sites within respective river basins. Seven species of clams, *Amblema costata, Corbicula manilensis, Elliptio crassidens, Lampsilis anadontoides, Lampsilis claibornensis, Megalonaias gigantea,* and *Plectomerus dombeyanus,* were collected from the stream systems. Samples consisted of one to four species. Since species varied in size, sufficient numbers of individuals were collected to provide 8–20 g for extraction.

The 13 sampling sites are shown in Figure 1. Collections were made by hand from shallow water; in deeper areas, dip nets, dredges, and oyster tongs were used. Clams were refrigerated and returned to the laboratory in ice chests. Specimens were then identified, and their soft tissues were removed. Soft tissues were blotted on Whatman No. 1 filter paper to reduce excess water and were frozen at —15°C until extraction could be performed.

Analysis

Pesticides were extracted from clams by a modification of the procedure outlined in *Analysis of Pesticides in the Aquatic Environment* (*8*). Each sample was combined with three times its weight of sodium sulfate and extracted twice with equal portions of redistilled hexane by blending 3 minutes each time. The procedure gave 92 percent recovery for the first extraction and 8 percent recovery for the second.

The extracts were combined and filtered through Whatman No. 1 and No. 3 filter papers. The resulting extract was partitioned into acetonitrile and evaporated to dryness in a Kuderna-Danish concentrator over a steam bath. The residue was dissolved in 25 ml hexane

FIGURE 1. *Mississippi River Basin sampling sites, for monitoring pesticide residues in freshwater bivalves, 1972–73. Stations 1–3: Yazoo River Basin; Station 4: Big Black River Basin; Station 5: Tombigbee River Basin; Stations 6–8: Pearl River Basin; Stations 9–13: Pascagoula River Basin.*

and subjected to Florisil column cleanup: 4 inches Na_2SO_4 bottom layer, 10 g Florisil, 3 inches Na_2SO_4 top layer, ether–hexane (15 + 85) elution mixture.

Water samples were also taken in conjunction with the clam samples. They were collected in glass jars which were sealed with aluminum foil-lined screw caps. Samples were refrigerated in ice chests and extracted upon return to the laboratory, as follows: One liter of unfiltered water was extracted with a 100-ml solution of 85 percent hexane and 15 percent petroleum ether by rolling 1 hr on a concentric rotator. The resulting extract was eluted through approximately 6 inch anhydrous Na_2SO_4 in a size 224 Chromaflex (Kontes, 1 inch ID) column using a mixture of hexane–ethyl ether (85 + 15). The extract was concentrated to 5 ml in a Kuderna-Danish apparatus over a steam bath.

All samples were analyzed on a Micro Tek 220 gas chromatograph equipped with ^{63}Ni electron-capture detector. Instrument parameters and operating conditions follow:

Columns:	6 ft × ¼ inch OD glass column packed with a mixture of 1.5 percent OV–17 and 1.95 percent QF–1 (1972 and 1973) 10 percent DC–200 (1972 only) 3 percent OV–1 (1973 only) each on Chromosorb W (AW, DMCS, HP)
Temperatures:	injector 220°C column 185–195°C detector 260°C
Carrier gas:	prepurified nitrogen flowing at ca 60–80 ml/minute

In 1973, a 3 percent OV–1 column was substituted for the 10 percent DC–200 because of its greater sensitivity and lower retention time.

Residues were qualitatively identified by comparison with a standard. Quantitative measurements were based on peak height and expressed in μg/g (ppm) for clam samples and μg/liter (ppb) for water samples. Results were not corrected for recovery.

Results and Discussion

Sites from which clams containing the highest levels of pesticides were taken corresponded with areas of greatest agricultural usage. Highest detectable levels of toxaphene and DDT and its metabolites were found in clams from sampling sites within the Yazoo, Big Black, and Tombigbee River Basins (Fig. 1). Watersheds of these basins are within the most highly exploited agricultural areas of Mississippi (Statistical Reporting Service, U.S. Department of Agriculture, 1973, personal communication). Pesticide residues were also detected in clams from the northern areas of the Pearl River Basin which drains farmlands. Clams from the Pascagoula River Basin contained the lowest levels of pesticides (Table 1).

Pesticide residues were not found in water samples collected during 1972. Residues of toxaphene and/or methyl parathion were detected in water samples collected during 1973 from sites within the Yazoo, Big Black, and Tombigbee River Basins (Table 2). Detectable levels of toxaphene and methyl parathion in water samples taken in 1973 reflect in part the increased use of these pesticides, following the limits imposed on use of DDT. The extreme insolubility of DDT in water may have precluded its detection in trace amounts in the 1972 samples.

Overall pesticide residues in clams from sites within the Yazoo River Basin were less in 1973 than in 1972 (Table 1). With respect to DDT, there were large-scale reductions of both *o,p'*-DDT and *p,p'*-DDT in clams. Residues of *p,p'*-TDE, a first-order breakdown product of DDT, remained constant or changed only slightly in 1973. Increases of *p,p'*-TDE coincided with subsequent decreases in *p,p'*-DDT levels. Residues of *p,p'*-DDE declined slightly or remained constant. Decrease in DDT, an increase in TDE, and an overall elimination of pesticides indicates that the clams may be metabolizing the DDT. This purging would have been accomplished when the entrance of DDT into the streams was reduced. Limited spraying or increased dilution would have caused such a reduction.

A second and possibly better explanation for the variations in observed levels of DDT and its metabolites would be runoff. It is well known that runoff is the strongest contributor of pesticides to streams which drain farmland. During the present two-year study, clams apparently assimilated greater amounts of TDE and lesser amounts of DDT as the levels entering the streams changed.

Flooding of the Mississippi River during Spring 1973, as well as limitations on DDT use, probably influenced these fluctuations of residues in clams throughout the Yazoo River Basin. Sampling sites within this basin are located near the area flooded and also drain more farmland than do any of the previously mentioned basins.

Toxaphene residues in clams were lower at most sites in 1973; however, residues in water increased. Water samples were taken near the surface, and increases in residues are probably the result of local spraying rather than runoff.

Reductions of all metabolites of DDT were observed at the sampling site within the Big Black River Basin. Levels of *p,p'*-TDE decreased, from 0.36 ppm to 0.09 ppm. Decrease in *p,p'*-DDT levels were even greater, from 0.67 ppm to 0.06 ppm; therefore, the same pattern was followed. The single sampling site from this

TABLE 1. *Comparison of 1972 and 1973 organochlorine residues in bivalves from major stream systems of the state of Mississippi*

	Residues µg/g															
	Chlordane		Endrin		Toxaphene		*p,p'*-DDE		*p,p'*-TDE		*p,p'*-DDT		*o,p'*-DDT		ΣDDT	
Yazoo Basin:	1972	1973	1972	1973	1972	1973	1972	1973	1972	1973	1972	1973	1972	1973	1972	1973
COLDWATER RIVER (QUITMAN COUNTY—R10W, T28N, 35)																
Corbicula manilensis	ND	ND	ND	ND	2.87	1.39	0.25	0.10	0.15	0.14	0.54	0.05	0.13	ND	1.07	0.28
Lampsilis anadontoides	ND	ND	ND	ND	TR[1]	0.48	0.08	0.04	0.06	0.04	0.11	0.02	ND	ND	0.25	0.10
SUNFLOWER RIVER (SUNFLOWER COUNTY—R4W, T18N, 8)																
Amblema costata	ND	ND	ND	ND	4.02	3.65	0.21	0.24	0.26	0.33	0.11	ND	0.53	0.22	1.11	179
Lampsilis anadontoides	ND	ND	ND	ND	4.86	1.51	0.28	0.12	0.27	0.16	0.22	ND	1.00	0.05	1.78	0.31
Plectomerus dombeyanus	ND	ND	ND	ND	1.01	0.75	0.05	0.10	0.10	0.14	ND	ND	0.08	0.03	0.23	0.28
STEEL BAYOU (ISSAQUENA COUNTY—R8W, T10N, 12)																
Amblema costata	ND	ND	ND	ND	1.09	0.72	0.12	0.18	0.13	0.16	ND	ND	0.07	0.01	0.32	0.26
Corbicula manilensis	ND	ND	ND	ND	7.68	3.62	0.39	0.23	0.40	0.49	ND	ND	0.53	0.10	1.32	0.81
Lampsilis anadontoides	ND	ND	ND	ND	1.93	1.11	0.18	0.11	0.21	0.21	ND	ND	0.12	0.04	0.51	0.35
Plectomerus dombeyanus	ND	ND	ND	ND	0.84	0.62	0.08	0.08	0.10	0.14	ND	ND	0.07	0.04	0.25	0.25
Big Black River Basin:																
BIG BLACK RIVER (WARREN COUNTY—R5W, T6N, 22)																
Corbicula manilensis	ND	ND	ND	ND	4.43	3.78	0.27	0.07	0.36	0.09	0.10	ND	0.67	0.06	1.40	0.22
Lampsilis anadontoides	ND	ND	ND	ND	TR[1]	1.01	0.04	0.02	0.05	0.03	ND	ND	0.06	0.02	0.14	0.06
Tombigee River Basin:																
TOMBIGBEE RIVER (LOWNDES COUNTY—R18W, T18S, 17)																
Megalonaias gigantea	ND	ND	ND	TR[1]	0.92	0.22	0.08	0.04	0.06	0.02	0.08	0.03	ND	ND	0.22	0.10
Pearl River Basin:																
PEARL RIVER (HINDS COUNTY—R1E, T6N, 36)																
Amblema costata	0.01	ND	ND	ND	ND	0.13	0.05	TR[2]	0.02	TR[2]	TR[2]	TR[2]	ND	ND	0.07	TR[2]
Lampsilis anadontoides	0.01	ND	ND	ND	ND	TR[1]	0.03	TR[2]	TR[2]	TR[2]	ND	ND	ND	ND	0.03	TR[2]
Plectomerus dombeyanus	TR[2]	ND	ND	ND	ND	0.13	0.02	0.01	TR[2]	TR[2]	ND	ND	ND	ND	0.02	0.01
Corbicula manilensis	ND	ND	ND	ND	ND	TR[1]	0.01	TR[2]	ND	TR[2]	ND	ND	ND	ND	0.01	TR[2]
Lampsilis anadontoides	ND	ND	ND	ND	ND	TR[1]	ND	TR[2]	ND	TR[2]	ND	ND	ND	ND	ND	TR[2]
PEARL RIVER (PEARL RIVER COUNTY—R18W, T5S, 29)																
Corbicula manilensis	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Pascagoula River Basin:																
CHUNKY RIVER (NEWTON COUNTY—R13E, T6N, 36)																
Corbicula manilensis	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Elliptio crassidens	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Lampsilis anadontoides	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
CHICKASAWHAY RIVER (WAYNE COUNTY—R7W, T8N, 10)																
Corbicula manilensis	ND	ND	ND	ND	ND	TR[1]	ND	TR[2]	ND	TR[2]	ND	TR[2]	ND	ND	ND	TR[2]
Elliptio crassidens	ND	ND	ND	ND	ND	0.30	ND	TR[2]	ND	TR[2]	ND	0.03	ND	ND	ND	0.03
LEAF RIVER (JONES COUNTY—R13W, T6N, 33)																
Corbicula manilensis	ND	ND	ND	ND	ND	TR[1]	0.04	0.02	0.05	0.01	0.05	0.02	ND	ND	0.13	0.05
Lampsilis anadontoides	ND	ND	ND	ND	ND	TR[1]	0.01	0.01	TR[2]	TR[2]	TR[2]	TR[2]	ND	ND	0.01	0.01
PASCAGOULA RIVER (GEORGE COUNTY—R8W, T2S, 23)																
Corbicula manilensis	ND	ND	ND	ND	ND	ND	TR[2]	TR[2]	TR[2]	TR[2]	ND	ND	ND	ND	TR[2]	TR[2]
Lampsilis anadontoides	ND	ND	ND	ND	ND	ND	ND	TR[2]	ND	TR[2]	ND	TR[2]	ND	ND	ND	TR[2]
Plectomerus dombeyanus	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
BLACK CREEK (GEORGE COUNTY—R8W, T3S, 14)																
Lampsilis claibornensis	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

NOTE: ND = None detected.
[1] Less than 0.1 µg/g for toxaphene.
[2] Less than 0.01 µg/g for DDT and metabolites.

TABLE 2. *Pesticide residues in water samples taken concurrently with Pelecypoda samples from major stream systems in the state of Mississippi, 1973*

Sampling site	Organochlorines	Residues, µg/liter (ppb)
Yazoo River Basin:		
Coldwater River (Quitman County—R10W, T28N, 35)	Toxaphene	0.46
	p,p'-DDE	0.01
Sunflower River (Sunflower County—R4W, T18N, 8)	Toxaphene	0.44
Steele Bayou (Issaquena County—R8W, T10N, 12)	Toxaphene	2.11
	Methyl parathion	0.25
Big Black River Basin:		
Big Black River (Warren County—R5W, T6N, 22)	Toxaphene	1.42
	Methyl parathion	0.46
Tombigbee River Basin:		
Tombigbee River (Lowndes County—R18W, T18S, 17)	Methyl parathion	0.08
Pearl River Basin:		
Three sampling sites	None detected	
Pascagoula River Basin:		
Five sampling sites	None detected	

basin is the lower end of the more highly agricultural, or Delta, region of Mississippi.

The single species collected from the Tombigbee River Basin, *M. gigantea*—a large species of clam whose soft parts weigh in excess of 300 g in mature adults—showed reduced levels of all pesticides except endrin between 1972 and 1973 (Table 1). Trace amounts of endrin were found in this species in 1973 but not in 1972. The Tombigbee River Basin drains away from the Mississippi River, thus agricultural lands are not as extensive as around the Yazoo and Big Black Basins. As anticipated in this large species from the Tombigbee River Basin, DDT and toxaphene levels were lower in 1972. Also, its residues were proportionately less reduced by 1973 than the residues in other, smaller species from the Delta basins. Since 300 g of tissue was too large an amount to be extracted by this procedure, 20 g of tissue consisting of approximately equal amounts from the gill, mantle, foot, and visceral mass were extracted. Reported levels may have varied slightly because of differences in the amounts of tissues extracted.

In the Pearl River Basin, 1973 residues of DDT and its metabolites in clams and water also decreased in areas where detectable levels had been found the previous year. Toxaphene residues in clams increased slightly (Table 1).

This Pearl River Basin, which is located south of the Delta region and east of the Mississippi River, receives fewer pesticides than the Yazoo, Big Black, or Tombigbee River Basins. The increase in toxaphene residues, although slight, is further evidence of the tendency of clams to reflect local fluctuations since no increases in toxaphene were observed in the flooded areas. Chlordane was found in clams in 1972 at one site on the Pearl River near Jackson, Mississippi (Fig. 1, No. 6), but was not found in 1973. Chlordane residues were very low and no residues of chlordane were detected in any other clam or water samples throughout the state.

Results of analysis of clams from the Pascagoula River Basin were similar to the Pearl River Basin results (Table 1). At Stations 10 and 12 (Fig. 1) slight increases in both toxaphene and DDT and its metabolites were recorded. These increases were between 0.005 µg/g and 0.01 µg/g in all but one sample (Table 1). On the Leaf River, Station 11, a decrease in DDT levels was observed between 1972 and 1973. This basin is the farthest from the Delta region, and residues were so low that no other trends in pesticide changes could be determined between 1972 and 1973.

A comparison of these increases and decreases in DDT residues in clams shows that *C. manilensis* is the best indicator of change. In every instance in 1972, *C. manilensis* contained the highest levels of DDT and toxaphene. In 1973, *C. manilensis* again showed the most substantial reductions (Table 1). This imported species, which is taxonomically, anatomically, and physiologically different from the Unionid species tested, might have a greater tendency to concentrate pesticides and a correspondingly greater ability to eliminate them.

Conclusions

Results indicate that freshwater clams are of value in reflecting changes in pesticide levels in streams. In areas where pesticides have been used for many years, once-a-year sampling programs may be sufficient to reflect changes in extremely residual pesticides, such as DDT. At all sampling sites within the Delta region of Mississippi, large reductions, not elimination, of DDT and its metabolites were recorded in clams between 1972 and 1973. In other areas of the state where pesticides were not expected because of lack of large agricultural operations, none were found; therefore the greatest contributor of pesticides to the streams of Mississippi is agricultural usage.

Although it is an indirect means of assessment, monitoring pesticides in freshwater clams may provide additional information on residue occurrence. Analysis of water is not reflective of biological concentrations.

Different species of clams also seem to have varying tendencies to concentrate and varying abilities to eliminate pesticides. *C. manilensis* is apparently the best indicator of the freshwater species sampled.

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Organochlorine and Heavy Metal Residues in Black Duck Eggs from the Atlantic Flyway, 1978 [1]

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ABSTRACT

Black duck (Anas rubripes) *eggs were collected during 1978 in the Atlantic Flyway. One egg from each of 49 clutches was analyzed for organochlorine compounds and mercury. DDE was detected in 39 eggs, ranging from 0.09 ppm to 3.4 ppm, wet weight. DDE residues were highest in eggs from Delaware, where the mean DDE level was 2.0 ppm. DDT and TDE were present at low levels in only five and four eggs, respectively. PCBs resembling Aroclor 1260 were detected in 24 eggs and ranged from 0.43 ppm to 2.9 ppm. Eggs from Massachusetts and Rhode Island contained an average of >1.0 ppm PCBs, but eggs from Nova Scotia, Pennsylvania, Maryland, and Virginia contained no detectable PCBs. Dieldrin, oxychlordane, and heptachlor epoxide were present in a few samples at low levels. Mercury was detected in 31 eggs, ranging from 0.07 ppm to 0.34 ppm, wet weight. Twenty eggs analyzed for chromium, copper, and arsenic contained averages of 0.64 ppm, 1.7 ppm, and 0.18 ppm, respectively. No geographic pattern was observed in these metal residue levels. Eggshell thickness (0.347 mm) was identical to the pre-1946 norm.*

Introduction

Concern over reports of a declining black duck (*Anas rubripes*) population in the Atlantic Flyway (*7, 11*) led to a survey of organochlorine pesticides in eggs of this species in 1964 (*13*). DDE averaged over 4 ppm in eggs from three states in that survey, and DDT was present in all eggs analyzed. Use of DDT in the United States had declined when another collection of eggs was made in 1971 to see if residues in black duck eggs had also declined (*9*). Although DDT had decreased and there was a general downward trend in DDE residues, individual eggs in 1971 still contained DDE levels comparable to those in 1964.

The egg collection was again repeated in 1978, almost six years after a virtual ban on use of DDT in the flyway. The 1978 survey was undertaken to determine trends in organochlorine pollutant loads, to gain information on heavy metal residues in black duck eggs, and to generally assess the relationship of these residues to population levels of black ducks in the Atlantic Flyway. The results are reported here.

Sample Collection and Preparation

In 1978, biologists in the Atlantic Flyway located and collected two eggs from each of 49 black duck nests. Eggs were individually wrapped in aluminum foil, packed in foam rubber, and shipped via air freight to the Patuxent Wildlife Research Center, Laurel, Maryland.

Egg measurements included weight, maximum length and breadth, and volume. Volume was measured by water displacement if eggs were whole, and by the formula $V = 0.506315LB^2 + 0.924992442$, where V = volume, ml; L = length, cm; B = breadth, cm, if eggs were cracked (*9*). Because dehydration or loss of lipid occurs in embryonated eggs, a specific gravity of 1.0 was assumed for all eggs, and residue values (ppm) were based on egg volume (*16*).

All dirt was cleaned off eggshells before they were opened at the equator and their contents extruded into a glass jar. Stage of embryonic development was noted and the contents were frozen until time for chemical analysis. One egg per clutch was analyzed for organochlorines and mercury (Hg). Twenty of these eggs were also analyzed for copper (Cu), chromium (Cr), and arsenic (As): two from Nova Scotia, three from Maine, three from New Hampshire, two from Massachusetts, four from Rhode Island, four from Delaware, and two from Virginia. Eggshells were washed with membranes intact and air-dried for two weeks. Four shell thickness measurements were taken at the equator with a Starrett 1010M micrometer with 0.01 mm graduations. The mean of these four values was considered the eggshell thickness for that egg.

Statistical comparison of residue levels in 1971 and 1978 were made, where possible, by a Student *t*-test. Since arithmetic and geometric means were nearly equal, arithmetic rather than geometric means were

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compared. Comparison of mean eggshell thickness measurements from pre-1946, 1964, 1971, and 1978 was made with one-way analysis of variance and Bonferroni multiple comparisons.

Analytical Procedures

ORGANOCHLORINES

Eggs were analyzed for *p,p'*-DDE, *p,p'*TDE, *p,p'*-DDT, dieldrin, heptachlor epoxide, oxychlordane, *cis*-chlordane, *trans*-nonachlor, *cis*-nonachlor, endrin, HCB, mirex, toxaphene, and polychlorinated biphenyl (PCB) residues. Egg contents were homogenized, mixed with anhydrous sodium sulfate, and extracted with hexane in a Soxhlet apparatus for 7 hours. Extracts were cleaned on a partially deactivated Florisil column (*1*). Pesticides and PCBs were separated on a SilicAR column into four fractions as described by Kaiser et al. (*8*).

Residues were quantified on a gas-liquid chromatograph equipped with a electron-capture detector and a column packed with a mixture of 1.5 percent OV–17 and 1.95 percent QF–1, under the conditions described by Kaiser et al. (*8*). Residues in three samples were confirmed on a Finnigan 4000 series gas-liquid chromatograph/mass spectrometer (*8*).

Recoveries of pesticides and PCBs from fortified chicken eggs averaged 94 percent. Residues reported here were not corrected for recovery. The lower limit of quantification was 0.1 ppm for all pesticides and 0.5 ppm for PCBs.

MERCURY

Eggs were homogenized in a Virtis blender, and a 5-g portion was taken for Hg analysis. Samples were digested by a method similar to that described by Monk (*12*). Mercury levels were determined by a cold vapor atomic absorption spectrometry method similar to that of Hatch and Ott (*4*), using a Coleman Model MAS 50 mercury analyzer. A portion of sample was added to a BOD bottle and diluted to 50 ml with water. Five milliliters of 10 percent hydroxylamine hydrochloride and 5 ml of 10 percent stannous chloride were added to the mixture to reduce Hg ions to metallic Hg. The sample was aerated and the Hg was measured in the air stream passing through a gas cell in the path of ultraviolet light at 253.7 nm.

Recoveries of Hg from spiked chicken liver samples averaged 93 percent. The lower limit of quantification was 0.02 ppm. Samples were not corrected for percent recovery.

COPPER, CHROMIUM, AND ARSENIC

A 5-g portion of each homogenized egg was dried for 2 hours at 110°C in a drying oven, then charred for 2 hours at 200°C in a muffle furnace. The temperature was raised to 600°C at a rate of 100°C/hour and the sample was left to ash overnight. The ash was cooled, dissolved over a hotplate in approximately 4 ml nitric acid and 1 ml hydrochloric acid, transferred to a 50-ml polypropylene centrifuge tube, and diluted to 10 ml with distilled deionized water. This solution was used for Cu and Cr analyses.

A 5-g aliquot was digested overnight at room temperature in 20 ml concentrated nitric acid. After an addition of 5 ml aqueous 1 percent Ni as $Ni(NO_3)_2$, the acid was slowly boiled away until the volume in the flask was approximately 1–3 ml. The remainder was transferred to a 50-ml polypropylene centrifuge tube and diluted to 25 ml with distilled deionized water. This solution was used for As analysis.

All heavy metal determinations were made by flameless atomic absorption spectrophotometry with a Perkin-Elmer 460 AAS instrument equipped with an EGA 2200 graphite furnace and accessory ramp, a deuterium arc background corrector, an AS 1 autosampler set for 20 μl injections, pyrolytically coated graphite tubes, and a PRS 10 printer. The furnace conditions were as follows:

Dry at 110°C for 40 seconds with 30-second ramp
Char at 900°C for 40 seconds with 30-second ramp
Atomize at 2700°C for 5 seconds with no ramp

The peak height mode was used with an integration time of 7 seconds.

The Cu and Cr determinations were made by comparison with aqueous standards at wavelengths of 324.7 nm and 357.8 nm, respectively, using hollow cathode lamps.

The As determination was made by the method of additions with the matrix modification of adding a 1 percent solution of Ni as $Ni(NO_3)_2$ to the furnace as described by Shum et al. (*14*). An electrodeless discharge lamp and wavelength of 193.7 nm were used.

The lower limits of quantification were 0.05 ppm for Cu and Cr and 0.1 ppm for As. Recoveries from fortified chicken livers ranged from 92 percent to 97 percent; residues were not corrected on the basis of these data.

Results and Discussion

ORGANOCHLORINES

DDE and PCBs were the only organochlorines detected in the majority of the 49 eggs analyzed (Table 1). DDE was present in 39 eggs; the average concentra-

TABLE 1. *DDE, PCB, and mercury residues in black duck eggs from the Atlantic Flyway, 1978*

Location Collection	No. of Clutches	p,p'-DDE	Aroclor 1260	Hg
CANADA				
Nova Scotia	3	0.32 ± 0.15[1] ND–0.58 (2)[3]	ND[2]	0.13 ± 0.03 0.07–0.16 (3)
New Brunswick	1	ND	0.60 (1)	0.14 (1)
Quebec	4	0.64 ± 0.45 0.19–2.0 (4)	0.25 ± 0.20 ND–0.84 (1)	0.12 ± 0.04 ND–0.21 (3)
UNITED STATES				
Maine	6	0.26 ± 0.19 ND–1.2 (4)	0.34 ± 0.29 ND–1.8 (1)	0.18 ± 0.05 ND–0.34 (5)
New Hampshire	5	0.32 ± 0.15 0.12–0.96 (5)	0.61 ± 0.31 ND–1.7 (3)	0.11 ± 0.03 ND–0.20 (4)
Vermont	4	0.44 ± 0.25 0.14–1.2 (4)	0.44 ± 0.23 ND–0.95 (2)	0.10 ± 0.01 0.08–0.14 (4)
Massachusetts	2	0.63 ± 0.37 0.26–1.0 (2)	1.1 ± 0.10 1.0–1.2 (2)	0.08 ± 0.01 0.07–0.09 (2)
Rhode Island	5	0.36 ± 0.05 0.25–0.50 (5)	1.3 ± 0.21 0.62–1.8 (5)	0.13 ± 0.04 ND–0.25 (4)
Pennsylvania	1	0.11 (1)	ND	0.08 (1)
Delaware	10	2.0 ± 0.25 0.84–3.4 (10)	0.98 ± 0.23 ND–2.9 (9)	0.09 ± 0.02 ND–0.30 (4)
Maryland	2	0.10 ± 0.02 0.09–0.12 (2)	ND	ND
Virginia	6	ND	ND	ND
Atlantic Flyway	49	0.65 ± 0.12 ND–3.4 (39)	0.56 ± 0.09 ND–2.9 (24)	0.11 ± 0.01 ND–0.34 (31)

[1] Arithmetic mean ± SE. Range of values appears under the mean.

[2] ND—Sample or samples analyzed were below the quantification limit of 0.1 ppm before correction for moisture loss. If no eggs from a sampling unit contained quantifiable residues, ND appears in table. If one or more eggs from the sampling unit contained quantifiable residues, ND samples were used in calculating means as 0.05 ppm. ND samples in flyway means also equaled 0.05 ppm.

[3] Numbers in parentheses are the number of samples containing quantifiable residue levels.

tion was 0.65 ppm DDE and the highest concentration was 3.4 ppm. Eggs from New Brunswick and Virginia contained no DDE. In the nine states and provinces where eggs were collected in both 1971 and 1978, DDE in eggs averaged 1.2 ppm and 0.80 ppm, respectively ($P > 0.05$). Eggs collected in Delaware in the 1971 survey averaged 5.9 ppm DDE and ranged up to 14 ppm. Eggs in the present survey averaged only 2.0 ppm DDE, a significant decrease ($P < 0.05$), and the highest residue level was 3.4 ppm. In contrast, eggs from Vermont contained comparable levels of DDE in 1971 and 1978. Mean DDE levels were 0.51 ppm in 1971 and 0.44 ppm in 1978; the highest DDE level detected was 1.0 ppm in 1971 and 1.2 ppm in 1978.

It would appear that although states with higher DDE levels in black duck eggs have shown decreases over the last seven years, those states with lower levels are still showing little decline.

The incidence of DDT residues in 1971 and 1978 samples varies significantly. DDT occurred at > 0.1 ppm in 31 of 61 eggs analyzed in 1971, but in only 5 of 49 eggs analyzed in 1978. Three of these eggs were collected in Delaware (0.09–1.3 ppm DDT) and two in Rhode Island (0.14 ppm and 0.17 ppm).

Low levels (0.10–0.15 ppm) of TDE were found in only four of the 49 eggs analyzed in 1978 (two from Delaware and one each from Maine and Quebec). In 1971, TDE was detected at levels > 0.1 ppm in 11 of the 61 eggs.

PCBs resembling Aroclor 1260 were detected in 24 of the 49 black duck eggs. They were not detected in eggs from Nova Scotia, Pennsylvania, Maryland, and Virginia. Average PCB values ranged from 0.25 ppm in Quebec to 1.3 ppm in Rhode Island. The highest PCB residue of 2.9 ppm was detected in an egg from Delaware. These residues cannot be quantitatively compared with 1971 residues because a different analytical technique was used; however, residues were generally lower and occurred in a smaller percentage of samples.

Dieldrin was found at low levels in ony two samples analyzed, one from Delaware (0.09 ppm) and one from Massachusetts (0.17 ppm). Heptachlor epoxide was detected in only one sample, collected in Rhode Island (0.14 ppm). Again these are not comparable to 1971 residue levels. The decreased incidence of residues is related to the increase of detection limit from 0.05 ppm to 0.1 ppm for dieldrin and from 0.01 ppm to 0.1 ppm for heptachlor epoxide. Dieldrin was detected at levels > 0.1 ppm in 13 of the 61 eggs analyzed in 1971 and heptachlor epoxide was present in only two of the 1971 eggs at this level. These residue levels cannot be quantitatively compared because of differences in analytical techniques, but low concentrations were observed in eggs from both surveys. Oxychlordane was present in one black duck egg from Maine (0.12 ppm), two eggs from New Hampshire (0.13 and 0.16 ppm), one egg from Massachusetts (0.08 ppm), and one egg from Maryland (0.05 ppm). No other organochlorine residues were detected.

HEAVY METALS

Mercury was detected in 31 of the 49 eggs analyzed (Table 1). The overall mean was 0.11 ppm Hg, and residues ranged up to 0.34 ppm. No Hg was detected in eggs from the two states, Maryland, and Virginia. Other state and province means ranged from 0.08 ppm in Massachusetts and Pennsylvania to 0.18 ppm in

Maine. These levels are below those usually associated with decreased hatchability or survival of young pheasants (*2, 15*) or mallards (*5, 6*). Captive black ducks on a diet of 3 ppm methylmercury produced eggs containing 4–6 ppm Hg, wet weight, and both hatching and survival of young were depressed (*3*). The residues observed in eggs from the 1978 field collection are below this effect level.

Chromium and copper were detected in all 20 eggs analyzed for heavy metals. Average residue levels (mean ± SE) were 0.64 ± 0.07 ppm Cr and 1.68 ± 0.10 ppm Cu. Arsenic was present in 18 of the 20 eggs analyzed; the average level was 0.18 ± 0.02. Eggs from different sampling sites contained comparable Cu, Cr, and As residues.

EGGSHELL THICKNESS

Eggshell thicknesses of black duck eggs collected before 1946, when DDT use became widespread, and in 1964, 1971, and 1978 are presented in Table 2. Eggshell thickness in 1978 eggs averaged 0.345 mm (N = 49 clutches). Eggs more than 1-week developed were eliminated from the analyses, since embryo development can affect eggshell thickness. The 36 clutches remaining showed an average thickness (mean ± SE) of 0.347 ± 0.003 mm. These eggs were used in comparing 1978 eggshell thickness to thickness during other years. The range of eggshell thickness in 1978 was 0.279–0.389 mm.

There was no difference in eggshell thickness between eggs collected before 1946 (0.347 mm) and those collected in 1978 (0.347 mm). Eggshells collected in 1971 were also of a thickness comparable to those collected before 1946 and during 1978. Eggshells collected in 1964, however, were 7.5 percent thinner than the pre-1946 norm, and significantly thinner ($P < 0.01$) than eggshells collected in 1971 and 1978. This decrease in 1964 eggshell thickness was perhaps associated with the higher DDE residues found in the black duck eggs during that 1964 survey. DDE has been shown to cause shell thinning and lowered reproductive success in captive black ducks (*10*).

TABLE 2. *Shell thickness of black duck eggs from the Atlantic Flyway*

Parameter	Date of Collection			
	Pre-1946	1964	1971	1978
Eggshell thickness[1] (mm ± SE)	0.347 ± 0.003[2]	0.321 ± 0.004[3]	0.343 ± 0.003[3]	0.347 ± 0.003
N	38[4]	37[5]	52[5]	36[5]
% decrease from pre-1946	—	7.5[6]	1.2	—

[1] Mean of four measurements at the equator, membranes intact, all eggs developed < 7 days.
[2] Data are from H. M. Ohlendorf and E. E. Klaas, U.S.F.W.S., personal communication, July 1979.
[3] Data are from Longcore and Mulhern (9) and J. R. Longcore, U.S.F.W.S., personal communication, July 1979.
[4] N = number of clutches from which all eggs were measured and a clutch mean determined.
[5] N = number of clutches, from which one or two eggshells were measured.
[6] Eggshell thickness is lower than in all other years, one-way analysis of variance, Bonferroni pair-wise comparisons, $P < 0.01$.

Summary

DDE and PCBs were the only organochlorines found routinely in black duck eggs collected in 1978. DDE had not decreased significantly from 1971 levels on a flyway basis, but residues in more heavily contaminated areas had decreased. Mercury was found at low (0.1–0.3 ppm) levels in the eggs and chromium, copper, and arsenic were detected at levels below 2.5 ppm. Eggshell thickness was comparable to pre-1946 measurements; organochlorine and mercury residues were below those associated with reproductive problems in captive waterfowl.

Acknowledgments

We thank all state, Provincial, and Federal biologists involved in egg collection. Doug Louk and Peter Brockdorff provided technical aid. H. Ohlendorf, E. E. Klaas, J. R. Longcore, L. J. Blus, and E. Dustman reviewed the manuscript.

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Significance of Organochlorine and Heavy Metal Residues in Wintering Shorebirds at Corpus Christi, Texas, 1976–77

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ABSTRACT

Organochlorine and heavy metal residues were determined in 103 shorebirds of seven species collected at Corpus Christi, Texas, during the winter of 1976–77 to evaluate their potential effects on population survival. DDE and polychlorinated biphenyls (PCBs) were detected in most samples. Chlordane isomers, dieldrin, toxaphene, and heptachlor epoxide also occurred, but less frequently. In general, organochlorine residues were low in skinned carcasses. Geometric means on a wet weight basis ranged from 0.25 ppm to 4.76 ppm for DDE and from 0.67 ppm to 6.64 ppm for PCBs; residues of the other compounds averaged less than 1 ppm in all instances. Mercury, lead, arsenic and vanadium occurred in all shorebird livers, and selenium and cadmium were detected in all kidneys. Residues of these metals, except selenium, were low in most tissue samples. Selenium averages varied from 1.77 ppm to 5.62 ppm (wet weight) in kidneys; residues in this range may be sufficient to inhibit reproduction or to induce other forms of toxicity, especially at the higher levels.

Introduction

During the winter, large numbers of shorebirds of many species use the mudflats and shallow inlets of the bays at Corpus Christi, Texas. The south shore of Nueces Bay is crowded with an industrial complex including oil refineries, a zinc-smelting plant, chemical plants, and other industries; agricultural lands encompass much of the northern shores of Nueces and Corpus Christi Bays (Fig. 1). Sediments from parts of the Bay system are heavily contaminated with zinc and cadmium (*9*), and eggs of some aquatic birds have high levels of DDE (D. H. White, unpublished data). Thus, the potential for pollution problems is high in this area because of industrial effluents and pesticide runoff from surrounding croplands. Conservationists have expressed concern that wintering birds in this area may be accumulating harmful levels of environmental contaminants. This study was conducted to determine the levels of organochlorine and heavy metal residues in tissues of wintering shorebirds and to evaluate the significance of contamination on population survival.

Collection Methods

Shorebirds were collected at opportune times from December 1976 through March 1977 at the locations listed by species on Figure 1. Birds were killed using 12-gauge #4 steel shot so that tissue analyses for lead would not be biased. Soon after collection, birds were tagged, placed individually in polyethylene bags, and stored frozen until they were prepared for analysis. A total of 103 shorebirds of seven species was collected for organochlorine and heavy metal analysis.

Analytical Procedure

Organchlorine analyses were conducted at the Patuxent Wildlife Research Center, Laurel, Maryland. Before analysis, the birds were skinned, and the feet, beaks, wingtips, and gastrointestinal tracts were removed. The kidneys and livers were saved for heavy metal analyses. The carcasses were homogenized in a food grinder and a 10-g portion was mixed with anhydrous sodium sulfate and extracted 7 hours with hexane in a Soxhlet apparatus. Lipids were removed by Florisil column chromatography. The procedures used were those described by Cromartie et al. (*3*), except that the organochlorines were separated into four fractions on the SilicAR column rather than three fractions to ensure the separation of dieldrin or endrin into an individual fraction (*10*).

The pesticides in each fraction were identified and quantified with a gas-liquid chromatograph equipped with an electron-capture detector and a 1.5 percent OV–17/1.95 percent QF–1 column. Recoveries of pesticides and PCBs from spiked samples averaged 94 percent; residues were not corrected for recovery. The lower limit of quantification was 0.1 ppm for all pesticides and 0.5 ppm for PCBs. All residues are expressed as ppm wet weight. Residues in 13 percent of

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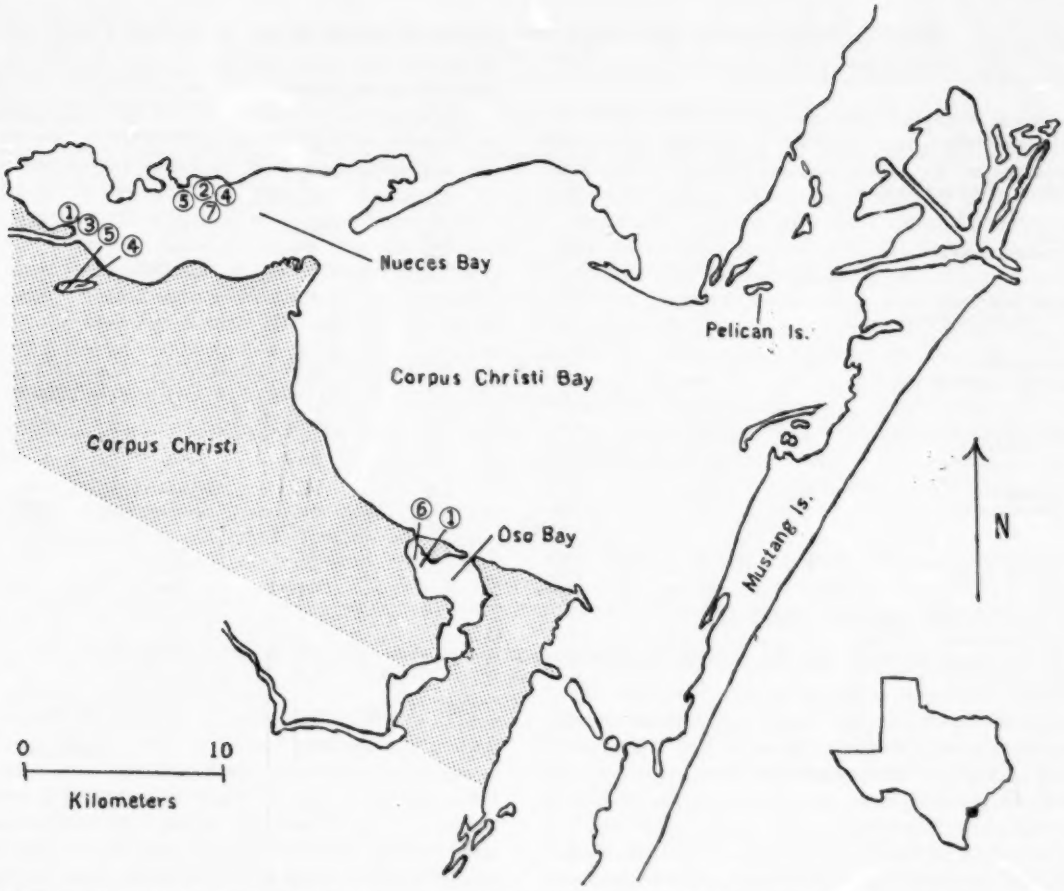

FIGURE 1. *Shore bird collection sites at Corpus Christi, Texas, 1976–77. Circled numbers represent sites for separate species; 1 = avocet, 2 = dunlin, 3 = greater yellowlegs, 4 = least sandpiper, 5 = lesser yellowlegs, 6 = sanderling, and 7 = western sandpiper.*

the samples were confirmed with a Finnigan 4000 series gas-liquid chromatograph/mass spectrometer.

Shorebird livers and kidneys were analyzed for certain heavy metals at Analytical Bio Chemistry Laboratories, Inc., Columbia, Missouri. Samples were shipped frozen in dry ice in chemically cleaned jars.

Samples were digested with 8 ml concentrated, double-distilled nitric acid for 4 hours on a reflux apparatus. Water condensers were used to condense the nitric acid during the digestion. Following digestion, the samples were diluted to 50 ml with 1 percent hydrochloric acid. A subsample of this digestate was further digested with nitric:perchloric acid to white fumes of perchloric acid. The sample digestate was then diluted to 25 ml with deionized water. The sample was then analyzed by atomic absorption or flame emission spectrophotometry. When graphite furnace techniques were used, solution concentrations were determined by the method of additions. Solution concentrations of those elements where flame techniques were used were determined by comparison of sample and standard peak heights. The standards contained approximately the same acid concentrations as the samples.

Analyses were conducted on a PE 305B atomic absorption unit with background correction. Graphite furnace analysis was performed on a PE MHS–10 hydride generation system. Recoveries of the various metals from spiked samples ranged from 74 percent to 106 percent; residues were not corrected for recovery. The lower limit of quantification was 0.1 ppm for mercury, lead, arsenic, selenium, and cadmium, and 0.05 ppm for vanadium. All residues are expressed as ppm wet weight.

Results and Discussion

ORGANOCHLORINE RESIDUES

Residues of DDE, PCBs, chlordane isomers, dieldrin, toxaphene, and heptachlor epoxide in shorebird carcasses are shown in Table 1. Mirex was present in only

TABLE 1. *Organochlorine residues in carcasses of wintering shorebirds from Corpus Christi, Texas, 1976–77*

Species	No.	Residues, ppm Wet Weight					
		DDE	PCBs	Chlordane Isomers	Dieldrin	Toxaphene	Heptachlor Epoxide
Avocet (*Recurvirostra americana*)	4	1.49[1] (4)[2] 0.5–2.6[3]	0.79 (4) 0.1–3.0	0.96 (2) 0.7–1.4	0.47 (3) 0.2–1.0	ND	ND
Dunlin (*Calidris alpina*)	13	3.15 (13) 1.0–9.0	1.19 (13) 0.5–8.0	0.12 (2) —	0.19 (7) 0.1–0.4	0.21 (5) 0.1–0.4	ND
Greater Yellowlegs (*Tringa melanoleucus*)	2	1.90 (2) 1.5–2.4	0.97 (2) 0.8–1.2	ND	ND	ND	ND
Least Sandpiper (*Calidris pusilla*)	30	1.07 (30) 0.2–4.6	0.67 (16) 0.8–3.6	0.16 (3) 0.1–0.7	0.16 (14) 0.1–0.6	0.19 (11) 0.1–0.5	0.32 (2) 0.2–0.5
Lesser Yellowlegs (*Tringa flavipes*)	17	4.55 (17) 1.7–9.0	0.79 (14) 0.5–1.8	0.13 (3) 0.1–0.2	0.16 (9) 0.1–0.3	0.29 (9) 0.2–0.7	0.14 (2) 0.1–0.2
Sanderling (*Calidris alba*)	15	4.76 (15) 1.6–10	6.64 (15) 2.4–18	0.66 (15) 0.2–1.7	0.28 (13) 0.1–0.6	0.14 (1) —	0.19 (14) 0.1–0.3
Western Sandpiper (*Calidris mauri*)	22	0.25 (17) 0.1–0.7	0.95 (22) 0.3–4.3	0.20 (7) 0.1–0.4	0.13 (8) 0.1–0.2	0.24 (9) 0.1–1.9	ND

NOTE: ND = not detected; — = not applicable.
[1] Geometric mean.
[2] Values in parentheses are actual number of samples containing detectable residues. These values were used in calculating means.
[3] Extreme values.

one sample at 0.53 ppm, but no other organochlorine compounds were detected in these samples. DDT metabolites were present in 95 percent of the samples analyzed, with most residues being identified as DDE. DDE concentrations were highly variable among individuals and species, ranging from 0.1 ppm to 10 ppm. Lowest overall DDE concentrations were found in western sandpipers (*Calidris mauri*) and the highest occurred in sanderlings (*Calidris alba*) (Table 1).

In general, DDE residue concentrations in shorebird carcasses were relatively low, and only moderately higher than levels measured in control birds in dietary experiments. Mallards (*Anas platyrhynchos*) fed diets containing 40 ppm DDE for 96 days averaged 33 ppm in carcasses 42 days after cessation of treated food; 11 months after DDE exposure, carcasses averaged 9.6 ppm in treated birds and only 0.5 ppm in controls (*8*). Black ducks (*Anas rubripes*) fed 10 ppm DDE for 7 months averaged 155 ppm in carcasses whereas controls averaged about 0.3 ppm (*12*); 2 years after exposure ceased, DDE levels in black ducks averaged 12 ppm in males and 3.4 ppm in females. Thus, it appears that shorebirds in the area sampled are being exposed to low environmental levels of DDE, if we assume that residue accumulation and loss is directly correlated with exposure (*20*).

PCBs occurred in 83 percent of the samples, ranging from 0.1 ppm to 18 ppm. As with DDE, PCB residue levels were highly variable among individuals and species (Table 1). The geometric mean of PCB concentrations in sanderlings was about seven-fold higher than in any other species; all the sanderlings were collected from Oso Bay (Fig. 1) near the outlet of a sewage treatment plant which may account for their elevated levels. Overall, PCB levels in shorebird carcasses were far below those levels known to cause death or reproductive problems in other avian species (*19*). Carcasses of great cormorants (*Phalacrocorax carbo*) suspected of dying from PCB poisoning contained residue concentrations ranging from 29 ppm to 460 ppm (*11*). Because PCBs are highly cumulative in avian tissues, as is DDE, we believe that shorebirds in the Corpus Christi area probably are being exposed to low environmental levels of these compounds.

Dieldrin occurred in only 52 percent of the samples and levels averaged less than 0.5 ppm in the 6 species where it was found (Table 1). Although dieldrin is much more toxic to birds than is DDE or PCBs, the present levels in shorebirds are not considered to be in the danger zone. Residue levels in carcasses of birds known to have died from dieldrin poisoning in experimental studies ranged from about 10 ppm to 36 ppm (*23*), much higher than the carcass levels reported in our study.

Chlordane metabolites including oxychlordane, *cis*-chlordane, *trans*-nonachlor, and *cis*-nonachlor were found in 32 percent of the samples, mostly in sanderlings (Table 1). Residues of all metabolites were low,

so they were combined for convenience and reported as *chlordane isomers*. Combined residue concentrations in individual samples ranged from 0.1 ppm to 1.7 ppm. All the sanderlings and 2 avocets (*Recurvirostra americana*) were collected from Oso Bay (Fig. 1) and this group of samples contained the highest chlordane residue levels; as stated earlier, the collection site in Oso Bay was near the outlet of a sewage treatment plant and the residues probably reflect domestic use of chlordane on lawns and gardens. Oxychlordane was the most persistent and the most toxic chlordane metabolite in bird-feeding studies (*21*). The levels in bodies of birds that died and in survivors were far above those reported in this study; therefore, the present levels are not suspected of contributing to shorebird mortality. The sublethal effects of chlordane to birds are unknown (*21*).

Heptachlor expoxide was present in only 17 percent of the samples and, as with other chlordane metabolites, occurred mostly in sanderlings (Table 1). Heptachlor epoxide found in bird tissues may be the result of exposure to either heptachlor or chlordane (*21*). Its adverse effects on wildlife have been documented (*20, 1*); however, the low levels we report for shorebirds are probably insignificant.

HEAVY METALS

Rsidues of certain heavy metals found in shorebird tissues are shown in Table 2. Livers were analyzed for mercury, lead, arsenic, and vanadium and kidneys were analyzed for selenium and cadmium. All the metals determined are known to be toxic to birds in sufficient quantities. All occur naturally in the environment; however, the burning of fossile fuels and many industrial, domestic, and agricultural uses of these elements contribute to abnormally high levels in some areas.

In dietary experiments, mercury has been shown to accumulate greatest in feathers, liver, and kidney (*7, 22*); uptake is rapid and loss is slow. A large proportion of the total body burden of mercury is eliminated in the feathers during molt (*22*). Most of the shorebirds that we analyzed were in full winter plumage; therefore, liver residues should give a fair indication of recent exposure levels. In general, mercury levels in our samples were considerably lower than those reported for some aquatic birds in other studies (*5, 6*), but were similar to those in shorebirds from a relatively unpolluted area in England (*16*). Mercury levels in our samples ranged from 0.05 ppm to 5.45 ppm, but most were below 0.5 ppm (Table 2). It is believed that these levels are below those suspected of causing toxic effects in other birds (*6*).

Lead residues in liver are considered indicative of current lead exposure, and levels that range between 6 ppm and 20 ppm (wet weight) or greater may be diagnostic of acute intoxication, at least in waterfowl (*13*). Only 3 birds in our study, all western sandpipers, were within this range and residue levels in all but 2 species averaged less than 0.2 ppm (Table 2). However, Dieter (*4*) suggests that birds with liver lead levels between 0.5 ppm and 1 ppm (0.86 ppm average) may exhibit abnormally low activity of plasma delta-aminolevulinic acid dehydratase, an enzyme important in the synthesis of hemoglobin and specifically inhibited by lead. Thirty-six percent of our samples contained lead residues within that range; sanderlings and western sandpipers had the highest residues. It is unknown whether these levels adversely affect shorebirds.

TABLE 2. *Heavy metal residues in livers and kidneys of wintering shorebirds from Corpus Christi, Texas, 1976–77*

Species	No.[1]	Residues, ppm Wet Weight					
		Mercury	Lead	Arsenic	Vanadium	Selenium	Cadmium
Avocet	4	0.22[2] 0.05–0.53[3]	0.11 0.05–0.19	0.10 0.05–0.26	0.02 0.02–0.05	2.60 2.20–3.90	1.82 0.79–8.20
Dunlin	10	0.47 0.28–0.78	0.19 0.05–0.58	0.07 0.05–0.35	0.06 0.03–0.16	3.55 2.40–5.00	1.94 0.52–7.30
Greater Yellowlegs	2	0.83 0.67–1.04	0.11 0.05–0.25	0.05 —	0.03 0.02–0.04	1.77 1.30–2.40	1.47 1.20–1.80
Least Sandpiper	16	0.50 0.11–1.69	0.17 0.05–1.28	0.06 0.05–1.50	0.07 0.03–0.23	4.23 1.60–6.90	4.31 0.83–22.7
Lesser Yellowlegs	13	0.21 0.11–0.73	0.18 0.05–1.17	0.10 0.05–0.42	0.04 0.02–0.16	2.43 1.50–4.20	1.33 0.44–2.60
Sanderling	15	0.67 0.12–5.45	0.93 0.24–2.01	0.14 0.05–1.23	0.07 0.02–1.20	3.96 2.10–6.40	1.38 0.33–7.90
Western Sandpiper	15	0.43 0.20–0.86	0.74 0.05–28.5	0.23 0.05–1.10	0.10 0.03–0.58	5.62 2.80–10.2	2.74 0.66–12.0

[1] All samples analyzed contained detectable levels of each metal. Livers were analyzed for mercury, lead, arsenic, and vanadium; kidneys were analyzed for selenium and cadmium.
[2] Geometric mean.
[3] Extreme values.

Arsenic is a major by-product of the smelting industry and a component of herbicides and defoliants used in agriculture (*14, 17*), thus the potential for abnormal arsenic accumulation in the environment appeared to be present in the Corpus Christi area. However, residue levels in our samples were quite low overall, averaging less than 0.3 ppm in all instances and ranging up to 1.5 ppm (Table 2). The significance of these low levels in shorebirds is unknown, but the levels probably reflect background contamination and are not suspected of being extremely harmful. Blus et al. (*2*) reported similar arsenic levels in livers of South Carolina brown pelicans (*Pelecanus occidentalis*).

Vanadium concentrations in livers were lowest of all the metals; residues averaged less than 0.1 ppm in most species (Table 2). White and Dieter (*24*) found that very little vanadium accumulated in tissues of mallard ducks fed up to 100 ppm vanadium in the diet; although vanadium accumulated in small amounts, tissue levels increased with treatment level. The liver levels we report here are similar to those reported for control birds in that study and are not suspected of being particularly harmful, overall. However, lipid metabolism may be altered in laying females when vanadium in the liver approaches 0.5 ppm (*24*). Several of our birds had levels of this magnitude.

Selenium levels in shorebird kidneys (Table 2) appeared to be abnormally high when compared with the results of a study involving chickens. Laying hens fed 5, 7, and 9 ppm selenium in the diet accumulated on the average about 2.5 ppm in the kidney while controls averaged less than 1 ppm (*15*). Reproduction was inhibited, especially in those hens fed 7 ppm and 9 ppm; significant decreases occurred in egg weight, egg production, and hatchability. Mean kidney levels in our study varied from 1.77 ppm to 5.62 ppm and ranged up to 10.2 ppm in individual samples (Table 2). Body burdens of this magnitude may be sufficient to impair reproduction in shorebirds as well, or cause other forms of toxicity. Since selenium is a by-product of the smelting industry, it is not surprising that levels in shorebirds from the Corpus Christi area appear abnormally high.

Cadmium residue levels in kidneys were highly variable in individual samples, ranging from 0.33 ppm to 22.7 ppm (Table 2). Mean levels were similar to those reported for ruddy ducks (*Oxyura jamaicensis*) and canvasbacks (*Aythya valisineria*) from the Chesapeake Bay area (*26, 28*) and are considered to be fairly low. Kidneys of mallards fed 2 ppm dietary cadmium contained an average of 1.5 ppm and 2.9 ppm after 30 days and 60 days, respectively (*25*); these levels also are similar to what we report here for shorebirds. Two hundred ppm dietary cadmium produced kidney lesions and inhibited spermatogenesis in adult mallards (*27*), but kidney cadmium levels averaged almost 100 ppm in these birds.

Conclusions

Shorebirds from the Corpus Christi area contained relatively low levels of each of the organochlorine compounds detected; experimental studies with other avian species suggest that these residues, in most instances, probably are below levels known to have an adverse effect on avian reproduction and survival. Some samples, however, did contain amounts of DDE or PCBs that approximate the range in which adverse effects may be expected. More important, shorebirds with fairly high residue levels may represent a potential hazard to peregrine falcons (*Falco peregrinus*) and other raptors that occasionally prey on them (*18*). Most residues of mercury, lead, arsenic, vanadium, and cadmium also were below known-effect levels. In contrast, selenium residues in shorebird tissues are cause for concern, because residues in most birds were within or above the range known to inhibit reproduction in chickens. In addition, the interactions of organochlorine and heavy metal residues in wild birds are poorly understood; birds with elevated total body burdens of a mixture of pollutants may be more susceptible to disease, stress, and predation than birds with low levels.

Acknowledgments

We thank Cathy Lefever and Christine Mitchell for technical assistance. Eugene Dustman and Lawrence Blus reviewed an earlier draft and their comments are appreciated. Clementine Glenn typed the manuscript.

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HUMANS

Overview of Human Exposure to Dieldrin Residues in the Environment and Current Trends of Residue Levels in Tissue

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ABSTRACT

An overview of available literature indicates that dieldrin residues are still found routinely in soil, air, water, and food, despite the 1974 U.S. Environmental Protection Agency ban on the use of aldrin and dieldrin. Dieldrin residue levels in environmental substrates, which are indicative of aldrin or dieldrin use, have decreased significantly since the mid-1960s, the peak usage years. However, human tissue studies do not show a corresponding decline in dieldrin residue levels. Thirteen studies, conducted between 1963 and 1976, show that average dieldrin levels in human adipose tissue and human milk fat remain between 0.160 ppm and 0.220 ppm. Other studies suggest that an equilibrium exists in the distribution of dieldrin among various tissues in humans, including blood, fat, brain, and liver. This relationship indicates that the concentration of dieldrin in any tissue may be used as an index of total body burden. Thus it appears that the concentration of dieldrin in the human body has reached a constant level at which the amount ingested and absorbed equals the amount metabolized and excreted. The mechanism of the stable concentrations is unknown, as are the possible health effects of chronic, low-level exposure to dieldrin.

Since the original inquiries into organochlorine toxicity and persistence in the 1960s, hundreds of studies have been conducted to determine the presence and effects of these pesticides in the environment and in humans. Organochlorines are unusually persistent due to the stability of their basic structural feature, the chlorinated ring. In virtually every study of residues in soil, air, water, and human tissue, two chemicals have stood out as particularly widespread: DDT and dieldrin. The U.S. Environmental Protection Agency (EPA) banned DDT for commercial use in the United States in 1972, and residue levels have since declined significantly (*26*). Dieldrin was banned in 1974. Despite this action, human exposure to dieldrin has not ended. Dieldrin residues are still found routinely in soil, air, water, and food.

Dieldrin reaches soil either directly, through intentional application, or indirectly, through rain or fallout from the air. Once incorporated with soil particles, dieldrin becomes so tightly bound that penetration through soil is negligible (*16*). Adsorption is determined primarily by soil type, although pH, temperature, and moisture content of the soil are also involved. Adsorption is strongest in soils with high clay or organic matter content. The high cation exchange capacity causes dieldrin to adsorb to negatively charged sites on the minerals (*21*). Lateral movement is insignificant, except under conditions of heavy erosion. Residues are stabilized, but they are not readily degraded. The half-life of dieldrin residues in soil is estimated to be 2.8 years, or eight years for 95 percent disappearance (*3*). Measurable residues are frequently apparent 11 years after original use. One study showed 10 percent of a subsoil application remaining 21 years after treatment (*2*). This tenacity is due in part to the paucity of soil organisms capable of decomposing dieldrin. To date, only 10 have been identified.

Calculations using the half-life given above and the annual sales data given in Table 1 indicate that if all dieldrin sold each year from 1960 to 1974 had been distributed evenly over all agricultural acreage in the United States, 0.074 pounds per acre would have accumulated in the soil by 1974—more than five times the amount actually applied that year.

Dieldrin residues circulate constantly from one storage medium to another. Although dieldrin adsorbs tightly to soil particles, small amounts may volatilize immediately after application, thus entering the atmosphere. Even slow volatilization from the tremendous surface area of treated soil and plants may contribute signifi-

[1] U.S. Environmental Protection Agency, Office of Pesticide Programs, Benefits and Field Studies Division (TS/768-M), Washington, D.C. 20460.

TABLE 1. *Domestic sales of aldrin and dieldrin (1,000 pounds), 1960–76*

Year	Aldrin	Dieldrin	Total	Literature Cited
1960	8,109	2,650	10,759	(46)
1961	9,926	2,764	12,690	(46)
1962	10,886	2,990	13,876	(46)
1963	12,152	2,685	14,837	(46)
1964	12,693	2,052	14,735	(46)
1965	14,278	1,814	16,092	(46)
1966	19,327	1,908	21,235	(46)
1967	18,092	1,473	19,565	(46)
1968	13,690	1,332	14,022	(46)
1969	9,902	1,206	11,108	(46)
1970	8,909	749	9,658	(46)
1971	11,615	705	12,320	(46)
1972	11,868	740	12,608	(46)
1973 (est.)	10,000	576	10,576	(46)
1974 (usage)	12,398	283	12,681	(45)
1976 (agr. usage only)	900		900	(15)

cantly to ambient air concentrations. After adsorption, the soil/dieldrin complex can be lifted and transported by wind erosion. These losses, however, are probably small compared to losses during application. Pesticide drift during treatment seems to be the primary factor influencing the transfer of dieldrin from soil to air (*14*).

Airborne pesticides have been detected near agricultural operations, in rural areas, at urban locations, and in wilderness regions many thousands of kilometers from known sources of contamination (*28*). The earliest indication that pesticide residues existed in the ambient air came from the analysis of air samples collected from four California sites during 1963 (*47*). Air monitoring conducted from 1970 to 1972 revealed that dieldrin was present in 94 percent of 2,479 samples taken nationwide, with a mean concentration of 1.6 ng/cu.m (*27*). Dieldrin levels as high as 29.7 ng/cu.m have been recorded at rural locations (*41*). The estimated residence time, i.e., rate of removal by dry deposition or rainfall, is 28 weeks (*1*).

Transport through air is probably the most important factor in the appearance of pesticide residues throughout the world. The detection of dieldrin residues at such remote sites as Barbados (*38*), the island of Bimini (*7*), and Antarctica (*43*) suggests that there may be no part of the troposphere that remains free of residues transported from distant sources.

Once in the air, dieldrin will eventually be deposited onto soil and surface water by rainfall or dust fallout. Through this process of deposition, erosion, and runoff, residues move through the hydrologic cycle. Rivers, lakes, and oceans act as sinks for pesticide residues collected through surface and underground runoff. The half-life of dieldrin in one cubic meter of surface water, that is, the time required for half the original deposit to be lost to the atmosphere, was found to be 1.5 years (*31*), or six years for 95 percent disappearance.

In a 1964–68 survey of pesticides in water, dieldrin dominated pesticide occurrences in all regions. It appeared in 39 percent of the samples (*29*). Several samples actually exceeded the environmental limit recommended by the Committee on Water Quality Criteria (*36*). In a second study, dieldrin was present in 40 percent of more than 500 drinking water samples taken from the Mississippi and Missouri Rivers (*40*). The extensive distribution of dieldrin in aquatic systems is indicative of environmental loading from nonpoint sources such as rainfall, dust fallout, and erosion, as well as from agricultural point sources (*36*).

Eventually, the small amounts of dieldrin in soil, air, and water collect in the plant and animal tissues that are food for humans. Dieldrin can be removed from the soil by various root crops, including sugar beets, carrots, radishes, and potatoes (*30*). Soybeans and peanuts, high in oil, may also contain residues (*4*). Lower concentrations are found in some cereal crops, corn, oats, barley, and alfalfa (*19*).

Food is probably the primary source of dieldrin residues in human adipose tissue. The Total Diet Studies of the Food and Drug Administration (FDA), U.S. Department of Health and Human Services provide exhaustive information on levels and exact dietary sources of many persistent pesticides. Dietary intake in the Total Diet Studies is based on the total food consumpton of a 15- to 20-year-old male. Unlike DDT, dieldrin concentrations do not differ with age, sex, or race (*13*), so this information applies to the general population.

According to the 1974 diet study, measurable dieldrin residues (greater than 1 ppb) occurred predominantly in meat, fish, and poultry (100 percent positive) and dairy products (97 percent positive) (*18*). This is due to the lipophilic properties of dieldrin. To avoid bioaccumulation of dieldrin residues, animal feed must be carefully monitored. Residues of 1 ppm in soil may be too high for crops destined for animal consumption (*19*). Garden fruits (60 percent positive), potatoes (30 percent positive), leafy vegetables (10 percent positive), oils and fats (10 percent positive), and fruits (7 percent positive) also contribute to man's daily intake.

The health effects of chronic low-level exposure to dieldrin are unknown. It is tremendously difficult to predict future effects on public health. Dieldrin is known to have carcinogenic, teratogenic, and reproductive effects on test animals (46). In one study, autopsies showed significantly elevated concentrations of dieldrin in patients who had suffered from portal cirrhosis, carcinoma of various tissues, and hypertension (*37*). Dieldrin is transferred to the fetus during pregnancy,

and the child receives additional doses after birth either from its mother's milk or from dairy products (*5*). Thus babies born after organochlorines came into common use may have stored substantial amounts of dieldrin within the first few months of life. Children and young animals are often more susceptible than adults to poisons, drugs, and carcinogens (*20*). The extreme persistence of dieldrin residues in the environment and in mammalian tissue may also cause health problems indirectly. In one case, dairy cattle, fed on hay from a field previously used as a cherry orchard to which dieldrin had been applied, produced milk exceeding acceptable dieldrin levels. The milk was withheld from market for three months until the residues dropped to acceptable levels (*34*).

The purpose of this study was to consolidate information from relevant reports on dieldrin residues in humans regarding the quantitative history of residue sources and concentrations, and to compare this information to the findings of EPA's *National Study to Determine Levels of Chlorinated Hydrocarbon Insecticides in Human Milk, 1975–76*. Data describing human exposure to dieldrin associated with the 1974 EPA ban were extracted to determine if any trends are appearing and how long residues may continue to appear in humans.

Evidence indicates that a dynamic equilibrium exists in the distribution of dieldrin among various tissues in humans, including blood, fat, brain, and liver (*23*). This functional relationship among tissues indicates that the concentration of dieldrin in one tissue is a function of the total amount of dieldrin in the body. Consequently, at least in the case of chronic exposures, the concentration of dieldrin in any tissue may be used as an index of the total body burden of dieldrin. Since dieldrin tends to concentrate in lipids, residue levels in human adipose tissue are frequently used to represent relative total body concentrations.

One of the easiest ways to obtain human fat is to extract milk from lactating women, since human milk contains 3–3½ percent fat. In 1975, EPA obtained 1,436 human milk samples for its *National Study to Determine Levels of Chlorinated Hydrocarbon Insecticides in Human Milk, 1975–76* (*44*). The study was carefully designed to include inhabitants of both rural and urban areas, as well as members of different socioeconomic groups, in order to provide a profile of dieldrin distribution in the United States. Residue levels were calculated on a fat-adjusted basis.

Dieldrin levels were ubiquitous in the human milk samples; 96 percent had residues greater than 1 ppb. The mean value of dieldrin in human milk was 0.164 ppm. These findings correspond closely to the results from the *1974 Survey of Pesticide Residues and Their Metabolites in Humans* (*26*), which showed dieldrin residues averaging 0.150 ppm in human adipose tissue. Thus it appears that fat-adjusted milk residue levels do represent a legitimate measure of total body burden. Dieldrin residues reflect exposure to both aldrin and dieldrin, because aldrin is quickly converted to dieldrin in the human body. Statistics on domestic sales of aldrin and dieldrin between 1960 and 1976 appear in Table 1. Dieldrin residues in adipose tissue from several locales between 1963 and 1977 are listed in Table 2. Studies of aldrin/dieldrin dietary intake between 1964 and 1975 are summarized in Table 3. Figure 1 charts data from all three tables.

Total aldrin and dieldrin sales increased constantly until 1966, then decreased until the EPA ban in 1974. The 1975 dietary intake was about 50 percent of that in 1966, the peak year (Table 3). Yet residues in human tissue have remained astonishingly constant. Thirteen studies from the United States, Canada, England, and Holland show dieldrin levels between 0.150 ppm and 0.220 ppm between 1963 and 1976 (*6, 26, 39, 48*).

Aldrin residues in food increased dramatically in 1975, after decreasing steadily since 1964. This increase may have been a result of the EPA ban itself. Since dieldrin is no longer manufactured in the United States, aldrin is important for registered use as a subsoil termiticide. An increase of aldrin residues in food would be expected to cause a corresponding increase of dieldrin residues in human tissues. However, no significant increase is apparent.

The exact cause of the unchanging concentrations is unknown. In view of the wide fluctuations in sales and dietary intake, simple persistence and biomagnification seem insufficient explanations. Hunter, et al. (*22*), after many years of research, concluded, that "the rates of increase of body burdens progressively decline in an asymptotic manner, the eventual body burdens being a characteristic of a person and his particular

TABLE 2. *Dieldrin residues in human adipose tissue, 1963–76*

Year	No. of Persons Sampled	% Positive	Mean, ppm	Location	Literature Cited
1963			0.15 ± 0.02	USA	(*6*)
1964			0.16	Canada	(*39*)
1966	47		0.21	England	(*39*)
1965–67	146		0.22	USA	(*39*)
1968	11	100	0.17	Holland	(*39*)
1970	200	100	0.20	USA	(*48*)
1970	1,412	97	0.18	USA	(*26*)
1971	1,615	99	0.22	USA	(*26*)
1972	1,913	98	0.18	USA	(*26*)
1973	1,094	99	0.18	USA	(*26*)
1974	898	99	0.15	USA	(*26*)
1975	779	96	0.17	USA	(*26*)
1976	682	94	0.15	USA	(*26*)

TABLE 3. *Adult dietary intake of aldrin and dieldrin in the United States, 1964–75*[1]

Year	% Positive Food Samples		μg/kg/day			μg/day			Literature Cited
	Aldrin	Dieldrin	Aldrin	Dieldrin	Total	Aldrin	Dieldrin	Total	
1964–65	5.6	18.5	0.01	0.08	0.09	1.0	5.0	6.0	(*11*)
1965–66	3.7	21.3	0.04	0.09	0.13	2.0	7.0	9.0	(*11*)
1966–67	3.3	15.3	0.01	0.05	0.06	1.0	4.0	5.0	(*11*)
1967–68	3.9	15.6	0.01	0.05	0.06	T	4.0	4.0+	(*9, 10*)
1968–69	1.4	25.3	0.0001	0.07	0.0701	T	5.0	5.0+	(*8*)
1969–70	0.8	31.3	0.0006	0.07	0.0706	T	5.0	5.0+	(*8*)
1970–71	—[2]	27.8	—[2]	0.0474	—[2]	—[2]	3.3	—[2]	(*33*)
1971–72	—[2]	23.6	—[2]	0.022	—[2]	—[2]	1.6	—[2]	(*32*)
1972–73	—[2]	27.5	—[2]	0.0470	—[2]	—[2]	3.2	—[2]	(*24*)
1973	0.3	29.7	0.0001	0.0403	0.0404	0.0057	2.8	2.8057	(*17*)
1974	0.3	25.8	0.0001	0.0441	0.0442	0.0064	3.1	3.1064	(*17*)
1975	0.4	23.3	0.0022	0.0387	0.0409	0.1500	2.6	2.7500	(*17*)

[1] All data on total food consumption for 15- to 20-year-old males.
[2] Data not available.

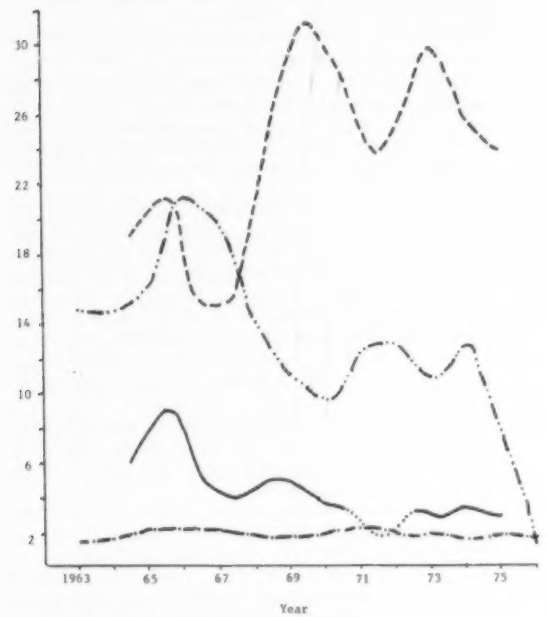

FIGURE 1. *Total domestic sales, percent positive food samples, total United States dietary intake, and human adipose tissue residues of aldrin and dieldrin, 1963–76*

Key: — — Food samples positive for dieldrin (%); — . . — Domestic sales of aldrin and dieldrin (million pounds); —U.S. dietary intake of aldrin and dieldrin (μg/day); . . . . . U.S. dietary intake of dieldrin only (μg/day); . — . — Dieldrin residues in international human adipose tissue (ppm × 10)

daily intake." Keane and Zavon (*25*), studying dogs, also found evidence supporting an "equilibrium hypothesis."

It appears that the concentration of dieldrin in the human body reaches a constant level at which the amount ingested and absorbed equals the amount metabolized and excreted. On the average, the maximum residue level maintained by the body seems to be in the range of 0.150 ppm to 0.220 ppm.

The metabolic process that allows the body to excrete

TABLE 4. *Number and proportion of nursing mothers with fat-adjusted levels of dieldrin greater than 100 ppb by the number of children previously breastfed*[1]

Number of Children Previously Breastfed	Total Number of Mothers	Number	Proportion
0	664	291	0.438
1	463	166	0.359
2	194	63	0.325
3	71	18	0.254
4	24	5	0.208
5 or more	20	5	0.250
TOTAL	1,436–N[2]	548–T[3]	0.382–p

[1] Reference *44*.
[2] N = Total number of mothers involved in the study.
[3] T = Total number of mothers with more than 100 ppb of the chemical in their milk.
[4] $p = T/N$ = proportion of mothers with level of the chemical higher than 100 ppb.

dieldrin when tissue concentrations reach a given level remains unclear. It does seem, however, that the total body burden of dieldrin in some way depends on the degree of obesity of the individual (*25*). A similar homeostatic mechanism has been described for DDT (*35*).

Of course, there may be any number of unidentified factors affecting the storage levels of dieldrin. Several implications have been made, but no definitive conclusions have been drawn. Some evidence suggests that rats fed diets containing DDT store less dieldrin than do control animals (*42*). Similar effects, if they occur in humans, could be counteracting normal decreases in dieldrin levels as environmental exposure to DDT declines in response to the 1972 EPA ban. Hundreds of other chemicals and drugs presently in use could also be affecting residue levels. A highly significant association ($P < 0.001$) between women with low levels of dieldrin in their milk and women who have nursed several children indicates that lactation is one form of organochlorine excretion (Table 4).

It is also possible that the contribution of respiratory intake to total body burden has been underestimated. Average respiratory intake of an adult during the workday is 1.75 cu.m/hr (*12*). Over a 24-hr period,

inhalation could add 1 μg to the daily intake if ambient air levels reached 20 ng/cu.m. Such levels have been recorded in agricultural areas. The possibility that current sampling techniques do not detect some portion of the pesticides in air must also be considered.

A thorough national drinking water survey has not yet been undertaken, so the contribution to dietary intake from water may be underestimated. The exposure of fetuses and very young children to dieldrin could create a whole generation of individuals with high residue levels, despite decreasing exposure during their lifetimes. Finally, one must consider the existence of pesticide reservoirs not yet identified by existing monitoring programs. Routes of transportation, storage, and degradation not yet quantified may exist.

All indications point toward the continuing presence of dieldrin residues in human milk and adipose tissue. Americans are still exposed to dieldrin constantly, through persisting contamination of soil, air, water, and, therefore, food. Evidence suggests that an equilibrium residue concentration is being maintained by most individuals at an average level between 0.150 ppm and 0.220 ppm. The maximum exposure level at which tissue levels will decrease below the equilibrium level is unknown. Further investigation is clearly required in this area as well as into potential influences on residue concentrations. Until the storage and homeostatic processes are fully understood, predictions regarding trends in human tissue residue levels will remain mere speculation.

Acknowledgment

The author gives special thanks to A. Hale Vandermer.

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WATER

Pesticides in Ground Water Beneath Irrigated Farmland in Nebraska, August 1978 [1]

Roy F. Spalding,[2] Gregor A. Junk,[2] and John J. Richard [3]

ABSTRACT

During the 1978 irrigation season, 14 ground water samples were collected in the Central Platte region of Nebraska, an area known to have high nitrate-nitrogen (NO_3–N) levels, and analyzed for the presence of 13 pesticide residues. Atrazine levels ranged from 0.06 μg/liter to 3.12 μg/liter and were correlated to NO_3–N concentrations with a coefficient of $r = +0.55$. Nitrate-nitrogen concentrations were measured as indicators of deep percolation from irrigated lands and ranged from 17.1 mg/liter to 34.3 mg/liter. Alachlor levels ranged from <0.01 μg/liter to 0.71 μg/liter. The amounts of 2,4-D were indeterminate because of experimental problems. Levels of the herbicides silvex and EPTC were below the limits of detectability. Levels of the organochlorine insecticides endrin, γ-BHC (lindane), dieldrin, DDT and its primary metabolite DDE, heptachlor and its primary derivative heptachlor epoxide, and methoxychlor were all below the detectable limits of 0.005–0.010 μg/liter.

Introduction

Monitoring of pesticides used currently in Nebraska has indicated that trace amounts of atrazine are infiltrating into the shallow ground water beneath well drained irrigated soils in Merrick County (*16*) and in the Platte River bottomland of Hall and Buffalo counties (*10*). In isolated cases, alachlor has also been found in ground water from the Platte River bottomland (*10*). In an agricultural state like Nebraska, where almost the entire population depends on subsurface sources for drinking water, knowledge of possible ground water contamination caused by vertical movements of pesticides through the unsaturated layer is imperative. Thus, the purpose of this study was to measure the levels of selected pesticides in ground water overlain by cropped and irrigated medium-textured silt loam soils having a moderately thick unsaturated layer. Most of the pesticides were selected because of current or past usage, but others were chosen because they have been mentioned in the *Federal Register* (*5*, *6*) in discussions on primary national drinking water regulations.

Ninety-four percent of the irrigated corn acreage in central Nebraska is treated with herbicides. Atrazine is the most frequently used herbicide in the study area, and alachlor is the second most widely used, according to Johnson and Byers (*9*). Alachlor is generally applied at pre-emergent rates of about 0.7 kg/ha as an alachlor/atrazine mixture.

2,4–D is used on less than 10 percent of the irrigated corn acreage and is applied after crop maturity at rates of about 0.5 kg/ha. Water solubility of over 900 μg/liter for both the acid and amine forms of 2,4–D and relatively low sorption characteristics suggest that some infiltration through well drained soils could occur.

EPTC and simazine are used for weed control only where shattercane is a problem. Usually this occurs on less than 3 percent of the corn acreage within the study area.

Silvex is not known to have been used within the study area but was measured because its use may be regulated in the future (*6*).

The γ-isomer of hexachlorocyclohexane (lindane) was one of the earliest used soil insecticides in the study area and was replaced by aldrin and heptachlor. Both

[1] Contribution from the Conservation and Survey Division, Institute of Agriculture and Natural Resources, University of Nebraska, Lincoln, Neb. This research was funded through grants from the Central Platte Natural Resources District, and was partially supported by the Ames Laboratory, U.S. Department of Energy, Contract No. W-7405-Eng-82, Division of Chemical Sciences (budget code AK-01-03-02-3).

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were used extensively for corn rootworm control until 1962 when emergence of resistant strains reduced their effectiveness. In the soil, aldrin and heptachlor are converted rapidly to dieldrin and heptachlor epoxide, respectively (*13*). The occurrence of dieldrin in ground water beneath Iowa cropland (*14*) and the occurrence of other insecticides in ground water beneath South Carolina cropland (*1, 15*) also prompted the measurement of these insecticides as probable indicators of past contamination.

The foliage insecticide DDT was applied extensively in the study area prior to 1962. Richard et al. (*14*) reported trace amounts of DDE in Iowa well water, and Achari et al. (*1*) and Sandhu et al. (*15*) reported that DDT and its metabolites were the most common pesticide residues in South Carolina ground water.

Methoxychlor and endrin were used either very sparingly or not at all within the study area but they were also mentioned in the *Federal Register* (*5, 6*).

Methods and Materials

SAMPLING

Water samples were collected in an area where NO_3–N concentrations in ground water exceeded 10.0 mg/liter (*7*). The well locations shown in Figure 1 are in an area where a low terrace borders the northern bottomland of the Platter River in central Nebraska. The terrace appears to be flat but does have a very gentle slope of 3.2 m/km, which is also the gradient of the east-northeast-flowing Platte River. The wells that were sampled are predominantly in irrigated areas of silt loam soils where corn is grown. Soils range from 1 m to 2 m thick and are underlain by an unsaturated layer composed of alluvial sand and gravel. Depth to ground water ranges from about 6 m on the southern edge of the terrace to slightly more than 10 m (*4*). Well depths are 20–23 m, which is near the boundary between the upper Pleistocene sand and gravel and the blue clayey silt. None of the wells penetrated into the Ogallala Formation, which lies beneath the clayey silt.

On August 1, 1978, water samples for NO_3–N and pesticide analyses were collected from the 14 irrigation well sites shown in Figure 1. If the well was not already being pumped at the time of sampling, about 20,000 liters of water were exhausted before the sample was collected.

ANALYSES

For the determination of NO_3–N, samples were collected in acid-cleaned, polyethylene bottles and were chilled until they were returned to the laboratory for filtration through 0.45-μm filters; filtered samples were refrigerated at 4°C until the time of analysis. Concentrations were determined by the automated cadmium reduction method of the American Public Health Association (*2*). The waters for pesticide analyses were not filtered. All pesticides were extracted from 4-liter samples, using XAD–2 resin, by the procedure of Junk et al. (*11*). Samples to be analyzed for the phenoxy herbicides were acidified in the field to a pH of 2.0 prior to extraction. Pesticide residues were analyzed by electron-capture gas chromatography and different polarity columns with periodic confirmation by GC/MS.

Results and Discussion

Detectable concentrations of atrazine occurred in all ground water samples, as shown in Table 1. Concentrations ranged from 0.06 μg/liter to 3.12 μg/liter. The significant correlation of +0.05 between atrazine and NO_3–N suggests that where the levels of NO_3–N are higher in the infiltrating water there are correspondingly higher amounts of atrazine. In an earlier study of another Central Platte area having very shallow depth

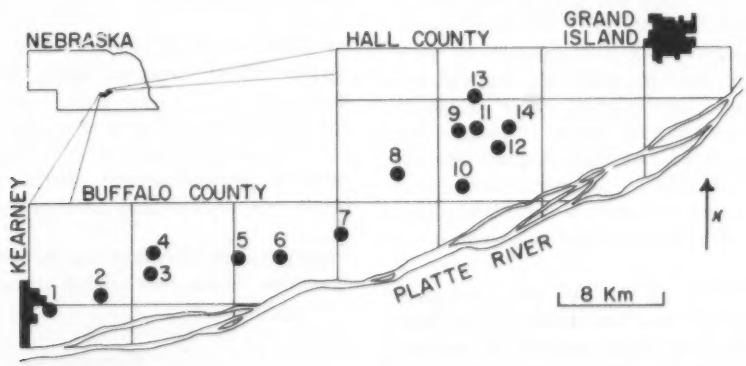

FIGURE 1. *Locations of the irrigation wells, sampled during August 1978 for pesticide analyses, in the Central Platte region, Nebraska, where the NO_3–N levels are >10 mg/liter and the sampled wells are assumed to be representative of over 1000 wells located within the study area.*

TABLE 1. *Pesticide and NO_3–N levels in ground water collected from irrigation wells in Central Nebraska, August 1978*[1]

Well No.	Legal Location[2]	Soil Texture[3]	Unsaturated Thickness, m	NO_3–N, mg/liter	Atrazine µg/liter	Alachlor µg/liter
1	8N–15W–5BB	si l	8.0	23.5	1.23	<0.010
2	9N–15W–35BC	si l	8.3	32.9	3.12	0.071
3	9N–14W–29BA	si l	9.3	34.0	0.82	<0.010
4	9N–14W–17CC	si cl l	8.3	34.4	1.41	0.018
5	9N–13W–19BB	si cl l	6.0	19.8	0.58	<0.010
6	9N–13W–21AB	l	6.0	10.9	0.16	<0.010
7	9N–12W–7CC	l	5.6	17.3	0.06	<0.010
8	10N–12W–27AC	si l	10.0	17.0	0.84	<0.010
9	10N–11W–8CC	si l	9.7	19.0	0.19	<0.010
10	10N–11W–32BB	si cl l	6.7	15.0	0.47	<0.010
11	10N–11W–9CB	si l	9.7	21.9	0.38	<0.010
12	10N–11W–15CD	si l	8.3	31.3	0.21	<0.010
13	11N–11W–33CC	si cl l	10.6	20.5	0.06	<0.010
14	10N–11W–11CD	si l	8.6	17.1	1.00	<0.010

[1] None of the other 11 pesticides searched for in these well waters were found above the detection limits in µg/liter of: 0.001 for lindane; 0.002 for heptachlor and heptachlor epoxide; 0.005 for endrin and dieldrin; 0.005–0.010 for DDE and methoxychlor; and 0.010 for DDT, EPTC, 2,4-D, and silvex.
[2] See Figure 1 for approximate geographical locations.
[3] si = silt; cl = clay; l = loam.

(<3 m) to ground water (*16*), the significant correlation between NO_3–N and atrazine appeared to be related to differences in soil texture such that higher concentrations were observed generally for ground water overlain by coarse-textured soils. The present data indicate that substantial amounts of atrazine move also in medium-textured soils and this vertical movement is not halted by unsaturated layers of 5.6–m to 10.6–m thickness.

Atrazine levels in ground water collected during the late summer of an irrigation season have been shown previously to be associated with vertical transport of atrazine applied during the same season (*10*). This being the case, an estimated 1 percent of the applied atrazine migrated vertically through the vadose zone (zone of aeration) to the ground water during the 1978 irrigation season. This estimate is based on an average atrazine concentration of 0.75 µg/liter, an average saturated zone thickness of 10.7–m depth with 20 percent porosity, and an average atrazine application rate of 0.75 kg/ha (*9*). Although this leakage estimate is close to that obtained by Lavy (*12*) for sandy loams in Nebraska, it is higher than that reported by Hall and Hartwig (*8*) for atrazine infiltration through silt loams in Pennsylvania. This greater vertical transport of atrazine in this area may be due to irrigation. The reason for the scatter in atrazine concentrations beneath irrigated farmland with soils of equivalent texture and similar unsaturated layer thickness is not obvious but may well be due to differences in water management.

Arachlor levels above 0.01 µg/liter in 2 samples suggest alachlor transport through medium-textured soils. Both samples contained relatively large amounts of atrazine, indicating that a formulation of the two compounds had been used on the upgradient fields.

The 2,4–D in these irrigation well waters could not be determined accurately due to some chromatography problems. However, all of the present data show 2,4–D levels below the detection limit of 0.05 µg/liter. This low level probably reflects limited usage in the study area and rapid degradation rather than poor transport, since Asmussen et al. (*3*) report 2,4–D to be one of the more mobile herbicides.

Concentrations of the herbicides EPTC and silvex in ground water were less than 0.01 µg/liter and 0.005 µg/liter, respectively. No simazine was detected even in waters that contained the highest levels of atrazine. This observation is consistent with the very limited use of these three herbicides within the study area.

Levels of γ-BHC, dieldrin, heptachlor, and heptachlor epoxide were below the limits of detection of 0.001, 0.005, 0.002, and 0.002 µg/liter, respectively. These insecticides have not contaminated the ground water, or have been sorbed efficiently to the aquifer sediments, or have degraded over the past 15 years since their use was discontinued.

All DDT and DDE concentrations were less than 0.01 µg/liter. These levels are similar to those reported by Richard et al. (*14*) for ground water in Iowa but are significantly lower than levels reported by Sandhu et al. (*15*) for ground water in South Carolina. The higher amounts probably reflect greater usage of DDT on cotton and soybean crop lands in that area.

Concentrations of endrin and methoxychlor were below detectable limits that varied from 0.005 µg/liter to 0.01 µg/liter.

Conclusions

Concentrations of pesticide residues in the ground water surveyed in the present study are well below the limits given in the interim primary drinking water

standards. The pesticide contamination of the ground water in the heavily irrigated study area in Nebraska is less than that reported for surface waters from New Orleans and Iowa (*14*) and for ground water from South Carolina (*15*).

Measurable amounts of atrazine in all samples, and alachlor amounts greater than 0.010 μg/liter in two samples, indicate that there is some vertical movement of the herbicides used extensively in the study area. The wide range in atrazine concentrations in water under predominantly silt loam soils suggests vertical transport associated with possible differences in water management. Whether this pesticide contamination of the ground water could be reduced or even eliminated with improved management is debatable.

Although the low levels of atrazine in the ground water are not toxic to humans, Wolfe et al. (*17*) report that the presence of atrazine and high amounts of NO_3–N in the ground water may evoke a further complication. They report formation of *N*-nitrosoatrazine in nitrogen-fertilized soils. Thus monitoring of nitrosamines and their probable precursors in the ground water of the Central Platte may be warranted.

Acknowledgments

Authors appreciate the helpful suggestions of M. E. Exner and R. Bentall and the technical assistance of J. Chow and M. Avery.

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APPENDIX

Chemical Names of Compounds Discussed in This Issue

ALACHLOR	2-Chloro-2',6'-diethyl-*N*-(methoxymethyl)-acetanilide
ALDRIN	Hexachlorohexahydro-*endo,exo*-dimethanonaphthalene 95% and related compounds 5%
AROCLOR 1254	PCB, approximately 54% chlorine
AROCLOR 1260	PCB, approximately 60% chlorine
ATRAZINE	2-Chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine
BHC (Benzene Hexachloride)	1,2,3,4,5,6-Hexachlorocyclohexane (mixture of isomers)
CHLORDANE	Technical: 60% octachloro-4,7-methanotetrahydroindane and 40% related compounds
2,4-D	2,4-Dichlorophenoxyacetic acid
DDE	Dichlorodiphenyldichloroethylene (degradation product of DDT)
DDT	Dichloro diphenyl trichloroethane. Principal isomer present (*p,p'*-DDT; not less than 70%): 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)-ethane
DIELDRIN	Hexachloroepoxyoctahydro-*endo,exo*-dimethanonaphthalene 85% and related compounds 15%
ENDRIN	Hexachloroepoxyoctahydro-*endo,endo*-dimethanonaphthalene
EPTC	*S*-Ethyl dipropylthiocarbamate
HCB	Hexachlorobenzene
HEPTACHLOR	Heptachlorotetrahydro-4,7-methanoindene
HEPTACHLOR EPOXIDE	1,4,5,6,7,8,8-Heptachloro-2,3-*epoxy*-3a,4,7,7a-tetrahydro-4,7-methanoindan
LINDANE	*Gamma* isomer of benzene hexachloride (BHC)
METHOXYCHLOR	2,2-Bis(*p*-methoxyphenyl)-1,1,1-trichloroethane 88% and related compounds 12%
METHYL PARATHION	*O,O*-Dimethyl *O*-*p*-nitrophenyl phosphorothioate
MIREX	Dodecachlorooctahydro-1,3,4-metheno-1*H*-cyclobuta[cd]pentalene
NONACHLOR	1,2,3,4,5,6,7,8,8-Nonachlor-3a,4,7,7a-tetrahydro-4,7-methanoindan
OXYCHLORDANE	1-*exo*-2-*endo*-4,5,6,7,8,8a-Octachloro-2,3-*exo*-*epoxy*-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene
PCBs (Polychlorinated Biphenyls)	Mixtures of chlorinated biphenyl compounds having various percentages of chlorine
SILVEX	2-(2,4,5-Trichlorophenoxy)propionic acid
SIMAZINE	2-Chloro-4,6-bis(ethylamino)-*s*-triazine
TDE	Dichloro diphenyl dichloroethane (1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane, principal component)
TOXAPHENE	Technical chlorinated camphene (67–69% chlorine)

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Articles are grouped under seven headings. Five follow the basic environmental components of the National Pesticide Monitoring Program: Pesticide Residues in People; Pesticide Residues in Water; Pesticide Residues in Soil; Pesticide Residues in Food and Feed; and Pesticide Residues in Fish, Wildlife, and Estuaries. The sixth is a general heading; the seventh encompasses briefs.

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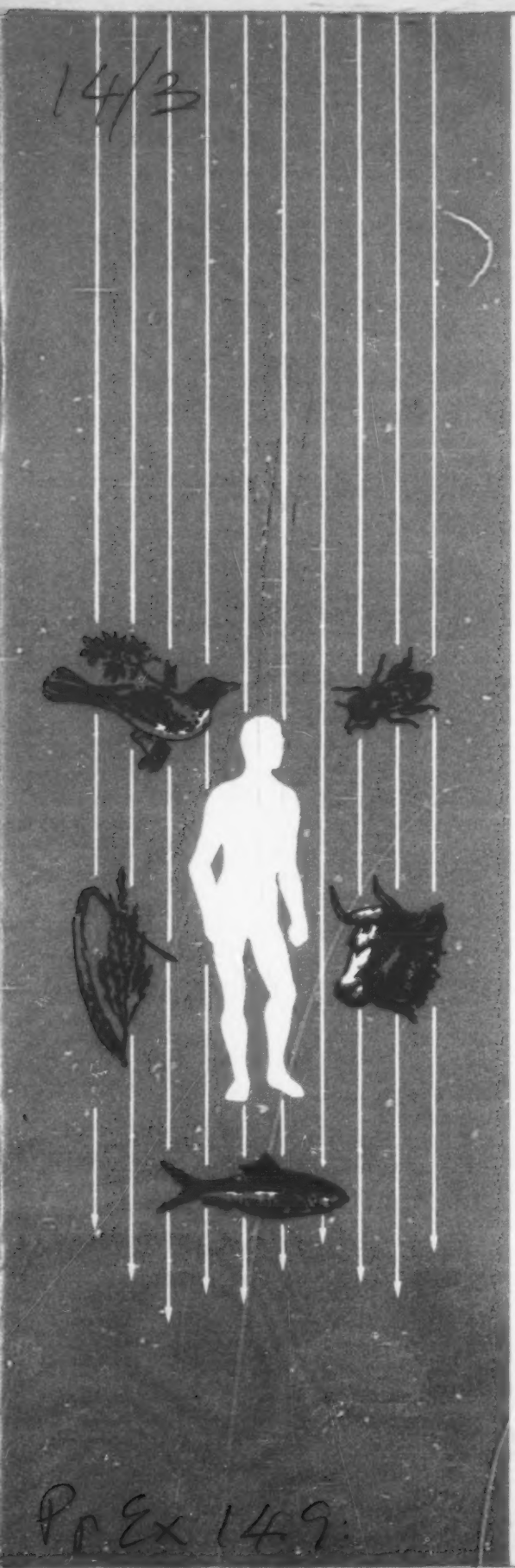

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The Working Group is comprised of representatives of the U.S. Departments of Agriculture; Commerce; Defense; the Interior; Health, Education, and Welfare; State; Transportation; and Labor; and the Environmental Protection Agency.

The Monitoring Panel consists of representatives of the Agricultural Research Service, Animal and Plant Health Inspection Service, Extension Service, Forest Service, Department of Defense, Fish and Wildlife Service, Geological Survey, Food and Drug Administration, Environmental Protection Agency, National Marine Fisheries Service, National Science Foundation, and Tennessee Valley Authority.

The *Pesticides Monitoring Journal* is published by the Chemical Information Division, Office for Program Integration and Information, Office of Pesticides and Toxic Substances, U.S. Environmental Protection Agency.

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SOILS

DDT Residues in Forest Floors and Soils of Western Oregon, September–November 1966

Duane G. Moore and Bobby R. Loper [1]

ABSTRACT

Between 1945 and 1965, 1.82 million hectares, or about 17 percent of the total commercial forestland in Oregon, were treated with 2.02 million kg DDT. Detectable residues of this insecticide might be present in forest soils, even those which have never received a direct application of insecticide. Forest floor and mineral soil samples were collected along four east-west transects across the Coast and Cascade Ranges. DDT residues were found in all samples, even though all but one site had never received a direct application of insecticide. In the Coast Ranges, mean concentrations of ΣDDT in forest floor samples were 0.049 ppm at the coast and 0.047, 0.064, 0.075, and 0.119 ppm at 16, 32, 48, and 64 km inland, respectively. Mean residue levels in the surface layers of mineral soil were much lower, 0.009 ppm and 0.006 ppm in the 0 to 7.5-cm and 7.5 to 15-cm depths, respectively.

Sampling sites along the Cascade Range transects were selected on the basis of elevation except that the eastern site of each transect was located 16 km east of the crest of the Cascades. Residue concentrations in forest floor samples were three to four times higher than in the Coast Ranges, but were still below 0.50 ppm. In general, ΣDDT levels increased with increasing elevation up to 1,372 meters and then decreased quite sharply east of the crest. Variations can be explained on the basis of total rainfall distribution and by transect location relative to agricultural and metropolitan centers.

Introduction

Intensified forest management is essential to meeting the ever-increasing demands for forage, recreation, timber, water, and of wildlife on our forested lands. The intensified use of our forest resources necessitated increased use of pesticides in insect, disease, and brush control programs. As a direct result, synthetic organic pesticides have become a chemical fact of life in forest protection and cultural practices.

Many pesticides in current use are rapidly detoxified in the forest environment. DDT, however, is highly resistant to degradation and may persist for extended periods of time. DDT is not currently registered by the U.S. Environmental Protection Agency (EPA) for use in forestry, but it has an extensive history of use and may be proposed to control specific pest outbreaks in the future. The present study was conducted to determine the levels and distribution of DDT residues in the forest floors and soils of western Oregon.

DDT was first applied to Oregon forests in 1945 to control an outbreak of the western hemlock looper in a 931-hectare (ha) aerial spray project near Cannon Beach (Fig. 1). Between 1945 and 1965, 1.82 million hectares, about 17 percent of the total commercial forestland in Oregon, were treated with 2.02 million kg DDT in various spray projects (Table 1). Applications were heaviest between 1949 and 1958 when 1.77 million hectares were treated in various spruce budworm spray projects.

Since 1958, about 104,682 ha have been treated with DDT, the latest project being carried out on 64,822 ha during 1974 under a Section 18 specific exemption from registration requirement granted to the Forest Service, U.S. Department of Agriculture, by the EPA.

DDT enters the forest floor and soil from direct application, drift of spray materials, rain washing through treated canopy, and litterfall, or in precipitation or dust deposited in unsprayed areas. Information on the extent of actual and potential environmental contami-

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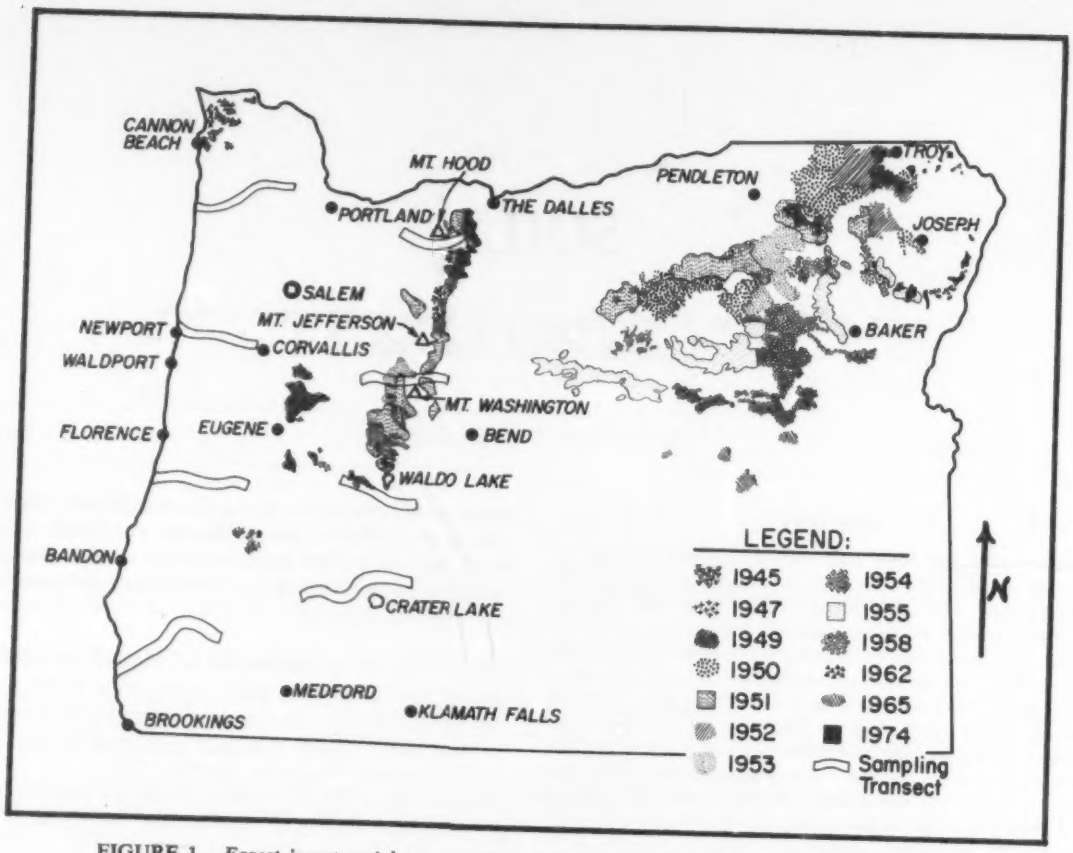

FIGURE 1. *Forest insect aerial spray projects in Oregon, and location of sampling transects*

TABLE 1. *Application of DDT to forests in Oregon, 1945–74*

Year	Hectares	DDT Applied, kg	
		By Year	Cumulative
1945	931	1,043	1,043
1947	5,666	6,350	7,393
1948	1,700	1,905	9,298
1949	109,508	122,742	132,040
1950	367,213	411,590	543,630
1951	319,986	358,656	902,286
1952	211,206	236,730	1,139,016
1953	149,815	167,920	1,306,936
1954	27,397	30,708	1,337,644
1955	251,270	281,636	1,619,280
1958	331,034	371,038	1,990,318
1962	13,152	7,371	1,997,689
1965	26,710	22,453	2,020,142
1974	64,822	54,492	2,074,634
TOTALS	1,880,410	2,074,634	

nation with pesticide residues in the forest is limited. Only a few studies have been concerned with ΣDDT. From a study conducted in a forest in New Brunswick, Canada, Woodwell (*26*) concluded that DDT residues would persist for a maximum of 10 years and that *o,p'*-DDT was leached into the subsoil. The forest had been sprayed with a total of 4.48 kg/ha of DDT between 1952 and 1958. Woodwell and Martin (*27*) reported that DDT residues in soils of heavily sprayed forests in Maine and New Brunswick had increased over a period of three years after the last application. They hypothesized that DDT residues persisted in the forest canopy and were carried to the soil by rain and litterfall.

A study in the same locality refuted Woodwell's suggestion that DDT residues were subject to differential weathering and preferential retention of *o,p'*-DDT (*28*). Yule reported that about 16 percent of the DDT originally applied still remained in surface soils after almost 20 years, and that the main component of the residue was *p,p'*-DDT. He also demonstrated that these DDT residues were unavailable to soil insects in toxic amounts (*28*).

The only environmental change reported from a study in northern Pennsylvania was a significant accumulation of DDT in the forest floor and surface soil (*6*). One year after aerial spraying at a rate of 0.56 kg/ha, no measurable increase in DDT residues was noted in fish, crayfish, or stream sediments. Belyea (*5*) measured DDT residues in soil and a related food chain in

northern Maine forests and concluded that the residues would disappear in 10–12 years. Riekerk and Gessel (*18*) reported that regardless of application rate, less than 1 percent of the DDT applied to the surface of a gravelly soil beneath a stand of Douglas fir (*Pseudotsuga menziesii* (Mirb.) Franco) leached through the surface soil over an 18-month period during which 100 cm of rainfall was recorded.

Tarrant et al. (*23*) conducted a long-term study of the behavior and fate of DDT in a forest environment in eastern Oregon after a 1965 aerial spray project. DDT residues were measured in throughfall precipitation, fresh litterfall, the forest floor and mineral soil, and in water samples from two streams draining the sprayed area. They reported that DDT residues in the forest floor had decreased by more than 50 percent after three years and had not leached into the mineral soil. Movement of DDT from the forest canopy to the forest floor was small and decreased with time. ΣDDT content of stream samples was only 0.3 ppb at the time of spraying, and this low concentration decreased rapidly to levels below the limit of detection. Only about one third of the applied chemical, however, was accounted for; 26 percent reached the forest floor initially, and another 6 percent reached the forest floor in litterfall over a three-year period. Their study did not measure the amount of DDT that had reached the forest canopy, and the extent of chemical loss from drift during spraying could not be assessed. It was assumed that a significant amount of chemical was lost to the atmosphere as drift during application or by volatilization from the canopy after spraying.

Other studies have reported the loss of significant amounts of insecticide to the atmosphere (*8, 11*). Acree et al. (*2*) demonstrated that there is significant codistillation of DDT with water at 25° to 35°C. Middleton (*15*) reported DDT residues as high as 1.71 g/1,000 cu. meters in the air adjacent to application sites. Two studies on the presence of organochlorine pesticides in rainwater were conducted in England, one in an agricultural area (*24*) and the other in London (*1*). Both studies reported detectable levels of *p,p'*-DDT and *p,p'*-DDE. Antommaria et al. (*3*) reported minimum concentrations of up to 1.14 μg/1,000 cu. meters for *p,p'*-DDT associated with suspended particulate matter in Pittsburgh, Pennsylvania, while Tabor (*22*) reported higher minimum concentrations of airborne DDT, up to 23 μg/1,000 cu. meters, mean of 4 μg/1,000 cu. meters, in agricultural communities.

Substantial use of DDT in the past, and research on deposition, persistence, and leaching characteristics of DDT, indicate that significant amounts of the insecticide may be present in the atmosphere. Rainfall and deposition of dust could result in detectable residue levels in forest soils, even those which have never received a direct application of DDT.

Sampling, Locations and Methods

The general areas sampled were the heavily forested sections of western Oregon. Sampling transects were selected in two subregions, the Coast and the Cascade Ranges. Four east-west transects were sampled in each subregion to cover western Oregon from north to south. In the Coast Ranges, sampling sites were located 0, 16, 32, 48, and 64 km inland along each east-west transect. Elevation was used to locate sampling sites in the Cascade Range. Sampling sites were located at 457, 762, 1,067, and 1,372 meters above sea level along each east-west transect across the Cascades. Sampling sites at the highest elevation, 1,372 meters, were approximately at the crest of the Cascades, and a fifth site on each transect was located 16 km east of the crest. This sampling site is in the rain shadow of the Cascade Range on each transect. Precipitation tends to decrease approximately 25 mm each 1.6 km eastward of the crest.

At each sampling site along the eight transects, four sublocations were sampled north, east, south, and west at 10, 20, 15, and 5 meters, respectively, of an arbitrarily located central point. At each point, the forest floor over a 0.4-sq. meter area was carefully removed, and approximately 1-kg samples of mineral soil were collected at each of two depths, 0 to 7.5 cm and 7.5 to 15 cm. Soil samples were collected by digging shallow soil pits and sampling horizontally into a freshly cleaned vertical face at the desired depth using a square-tipped, flat spade.

Extreme care was taken to avoid contaminating the lower sample with material from above, and all tools were cleaned between samples with acetone. Forest floor samples were placed in new, 10-kg heavyweight Kraft bags, and soil samples were placed in standard soil sample bags. All samples were stored during the day in portable cooler chests and frozen the same day they were collected. In all, 160 sublocations were sampled along the eight transects, resulting in a total of 160 forest floor samples and 320 soil samples. Sampling was accomplished over a three-month period, September–November 1966.

Analytical Procedures

Soil samples were air-dried, ground to pass a 10-mesh sieve, mixed, and subsampled. Forest floor samples were essentially dry when collected, having been collected at the end of the dry season; those containing some moisture were air-dried. All were processed carefully by hand to remove stones, and were then ground in a large Wiley mill. The ground samples were mixed and subsampled for analysis. After being ground and

mixed, the samples were held at 0°F until they could be subsampled and analyzed.

EXTRACTION

Soils—A 100-g subsample was extracted with hexane–acetone (41+59 azeotropic) in a Soxhlet extractor for 16 hr (*16*).

Forest Floor—A 25-g subsample was extracted with acetone in a Soxhlet extractor for 16 hr.

CLEANUP

The soil and forest floor extracts were transferred to individual separatory funnels and water was added to form a water–acetone (2+1) solution. The pesticides were partitioned into hexane by shaking with three 100-ml aliquots of hexane (*10*).

The hexane extracts were dried with anhydrous sodium sulfate, evaporated to 5–10 ml, and transferred to a 15-g Florisil column (*25*). The pesticides were eluted from the column with 100 ml dichloromethane–hexane (1+3). Dichloromethane was removed by evaporation, and samples were transferred with hexane to volumetric flasks for analysis.

ANALYSIS

The concentrations of DDE, *o,p'*-DDT, TDE, and *p,p'*-DDT were quantified in a MicroTek 2000 MF gas chromatograph with a 130-mc tritium electron-capture detector. This system gave good individual peak resolution at the following retention times: DDE, 5.2 minutes; *o,p'*-DDT, 6.8 minutes; TDE, 8.0 minutes; and *p,p'*-DDT, 9.5 minutes. Other instrument parameters and operating conditions were:

Column:	Pyrex, 180 cm × 2 mm ID, packed with 5 percent QF-1 (first 126 cm) and 5 percent DC-11 (last 54 cm) on 60–80-mesh Gas Chrom Q, preconditioned for 48 hr at 220°C	
Temperatures:	column	185°C
	detector	190°C
	injector	205°C
Carrier gas:	Nitrogen flowing at 30 ml/minute	

Minimum residue levels for quantitative determinations were 0.001 ppm for soil and 0.01 ppm for forest floor. Average percent recovery and range for DDT isomers and metabolites were as follows:

Form of DDT	% Recovery (Range)	
	Soil	Forest Floor
DDE	99 (92–103)	97 (93–100)
o,p'-DDT	82 (71–99)	99 (96–100)
TDE	82 (78–91)	85 (80–84)
p,p'-DDT	97 (92–100)	94 (90–97)

CONFIRMATION

Some industrial pollutants are similar to DDT in structure and properties and can interfere with its detection or identification (*12, 14, 17, 19, 20*); naturally occurring plant or soil substances may also cause analytical errors (*9, 13*). To confirm apparent DDT residues in the present study, about half the samples were analyzed by gas-liquid chromatography (GLC) with a chloride-specific, microcoulometric detection system. This step confirmed that substances with the same retention time as the DDT standards detected by the electron-capture detector did contain chlorine, but did not rule out the possible misinterpretation of polychlorinated biphenyls (PCBs) as DDT isomers and metabolites. Therefore, all samples analyzed with the microcoulometric detector were hydrolyzed with alcoholic potassium hydroxide which would chemically alter DDT and TDE, but not PCBs (*10*). Hydrolyzed samples were then re-analyzed by both electron-capture and microcoulometric detection systems. TDE, *o,p'*-DDT, and *p,p'*-DDT peaks disappeared after hydrolysis, indicating that PCBs were not present in detectable quantities and that the quantitative measurement of DDT isomers and metabolites by the electron-capture detection system was correct.

Mass spectrophotometry is the most positive means of identifying pesticides in biological samples, but in the present study, only the forest floor samples and a few of the soil samples contained sufficient DDT to allow use of this technique. Ten forest floor and two soil samples were extracted and purified for analysis. The DDT isomers and metabolites were separated by chromatography of the final hexane extract on 500-μm silica gel H thin-layer plates developed with benzene–hexane (4+96). DDT standards were co-chromatographed on both edges of the 20 × 20 cm plates. After development, a 15-cm strip in the middle of the plate was covered, and the DDT standards were located by spraying the edge of the plate with 0.5 percent silver nitrate and exposing the plate to ultraviolet light for 15 minutes. The *o,p'*-DDT, *p,p'*-DDT, and *p,p'*-DDE were scraped from the appropriate section of the center of the plate, extracted from the silica gel with hexane, and analyzed by electron-capture gas chromatography. The pesticides separated by the thin-layer method had the same retention times as the standards.

Extracts containing the individual pesticides were introduced into a Varian MAT Model CH 7 mass spectrometer with a direct inlet probe. The mass spectra for *o,p'*-DDT, *p,p'*-DDT, and *p,p'*-DDE isolated from the forest floor samples agreed with spectra of appropriate standards and with published spectra (*21*). A comparison of sample spectra with published PCB spectra (*4*) showed that no PCBs were present in the isolated pesticides. All confirmation steps gave positive evidence that the isolated and measured substances were indeed

DDT isomers and metabolites and that PCBs were not present in detectable quantities.

Results and Discussion

COAST RANGE TRANSECTS

DDT residues were found in all samples, even though all but one site had never received a direct application of insecticide. Mean concentrations of ΣDDT residues in the forest floor were 0.049 ppm at the coast and 0.047, 0.064, 0.075, and 0.119 ppm at 16, 32, 48, and 64 km inland, respectively, over all four transects (Table 2). These DDT residue levels were quite low and tended to increase progressively from the Oregon coast inland across the coastal mountain range to the western edge of cultivated inland valleys. The two northern transects terminate in forested areas adjacent to the Willamette Valley. No major insect control projects have been conducted in the coastal mountain areas of western Oregon, and the only source of DDT which could have produced these residues appears to be aerial drift from agricultural applications and municipal spray programs for control of mosquitoes and other insect pests.

TABLE 2. *ΣDDT residues in forest floors and soils of Coast Range transects of western Oregon, September–November 1966*

Transect	Sample Depth, cm	Residues, ppm[1] Distance from Coast, km 0	16	32	48	64	Transect Means
Wilson River	Forest floor	0.052	0.056	0.058	0.058	0.132	0.071
	Soil: 0–7.5	0.005	0.005	0.006	0.009	0.024	0.010
	Soil: 7.5–15	0.006	0.011	0.013	0.003	0.006	0.008
Yaquina	Forest floor	0.037	0.038	0.081	0.098	0.116	0.074
	Soil: 0–7.5	0.007	0.013	0.006	0.009	0.009	0.009
	Soil: 7.5–15	0.006	0.005	0.005	0.004	0.005	0.005
Umpqua	Forest floor	0.054	0.046	0.060	0.054	0.130	0.069
	Soil: 0–7.5	0.006	0.006	0.008	0.008	0.013	0.008
	Soil: 7.5–15	0.004	0.004	0.005	0.007	0.008	0.005
Rogue	Forest floor	0.054	0.049	0.058	0.093	0.098	0.070
	Soil: 0–7.5	0.004	0.011	0.007	0.007	0.012	0.008
	Soil: 7.5–15	0.005	0.006	0.005	0.006	0.010	0.006
Site means	Forest floor	0.049	0.047	0.064	0.075	0.119	0.071
	Soil: 0–7.5	0.005	0.009	0.007	0.008	0.015	0.009
	Soil: 7.5–15	0.005	0.006	0.007	0.005	0.007	0.006

NOTE: ΣDDT residues include *p,p'*-DDE, *o,p'*-DDT, TDE, and *p,p'*-DDT. TDE could not be quantified in all samples.
[1] Each value represents the mean total residue for four samples from that site on the transect.

Contamination of the forested areas is surprisingly uniform along the four transects, the highest residue levels occurring adjacent to areas of agricultural activity and population centers in the inland valleys and then decreasing toward the coast with greater distance from the source. Mean annual precipitation varies from 114 cm to 265 cm between the sampling points, but there is no apparent correlation between residue levels and amount of precipitation ($r = 0.16$). Even the lowest amount of precipitation was apparently adequate to bring down any aerially transported residues to the forest floor.

Residue levels of ΣDDT in samples of the surface layers of mineral soil were much lower than levels found in forest floor samples, with average concentrations of 0.009 ppm and 0.006 ppm in the 0 to 7.5- and 7.5 to 15-cm depths, respectively. Residue levels in the mineral soil showed similar but less pronounced trends in distribution compared to those observed in the forest floor. Residues reaching the forest floor were not readily leached into the mineral soil. More than 80 percent of the ΣDDT residues reaching each site remained in the forest floor.

CASCADE RANGE TRANSECTS

Residue levels of ΣDDT in the forest floor and soils at sampling sites along the east-west transects across the Cascade Range in western Oregon appear in Table 3. These sites were selected on the basis of elevation except that for the eastern site on each transect, a location 16 km east of the crest of the passes through the Cascades was selected in order to determine whether the rain shadow had any measurable effect on the level of DDT residues in the forest environment. Residue concentrations in the forest floor were three to five times higher than those found in the Coast Ranges, but were still below 0.50 ppm. Trends in residue distribution patterns are not very distinct, but in general, total residues levels increased with increasing precipitation ($r = 0.67$) and decreased quite sharply east of the crest.

TABLE 3. *ΣDDT residues in forest floors and soils of Cascade Range transects of western Oregon, September–November, 1966*

Transect	Sample Depth, cm	Residues, ppm[1] Elevation above Sea Level, Meters 457	762	1067	1372	16 km East[2]	Transect Means
Mt. Hood	Forest floor	0.344	0.433	0.326	0.417	0.271	0.358
	Soil: 0–7.5	0.010	0.009	0.010	0.011	0.013	0.011
	Soil: 7.5–15	0.006	0.007	0.005	0.006	0.010	0.007
Santiam Pass	Forest floor	0.330	0.268	0.391	1.405[3]	0.147	0.508
	Soil: 0–7.5	0.022	0.010	0.013	0.081	0.011	0.027
	Soil: 7.5–15	0.012	0.005	0.006	0.008	0.006	0.007
Willamette Pass	Forest floor	0.383	0.425	0.298	0.225	0.059	0.278
	Soil: 0–7.5	0.010	0.047	0.018	0.005	0.005	0.017
	Soil: 7.5–15	0.007	0.010	0.008	0.004	0.003	0.006
Crater Lake	Forest floor	0.111	0.110	0.138	0.192	0.105	0.131
	Soil: 0–7.5	0.013	0.012	0.007	0.007	0.008	0.009
	Soil: 7.5–15	0.005	0.007	0.004	0.005	0.006	0.006
Site means	Forest floor	0.292	0.309	0.288	0.560	0.145	0.319
	Soil: 0–7.5	0.014	0.020	0.012	0.026	0.009	0.016
	Soil: 7.5–15	0.007	0.007	0.006	0.006	0.006	0.006

[1] Each value represents the mean of four samples at that site.
[2] Eastern sampling point was located 16 km east of the crest of the Cascades.
[3] This sampling site by chance fell in an old spray unit treated in 1953.

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Residue levels in the forest floor samples from the Cascade Range varied considerably between sampling sites along each transect, and even between sublocations at each site. This variation can be attributed largely to old spray projects which took place along the crest of the Cascades from Mt. Hood on the north to Waldo Lake on the south (Fig. 1). Only one sampling site was located in an area that had been sprayed with DDT, but several others were close to an old spray project or were at locations that may have received drift from more than one spray application. Spray projects were conducted along the crest of the Cascades every year from 1949 through 1953, and 1.16 million hectares were treated with a total of 1.30 million kg DDT. None of the treated areas was included in more than one control project, but adjacent units were sprayed in consecutive years. The sampling site at 1,372-meter elevation on the Santiam Pass transect was sprayed in 1953, and 13 years later the forest floor at this site still contained an average concentration of 1.405 ppm ΣDDT. The low mean annual temperature at this high-elevation site would greatly reduce the rate of normal degradation.

Levels of ΣDDT residues in the surface of 7.5-cm layer of mineral soil are almost double the concentration found at the same depth in the Coast Range samples, but the mean concentrations at the 7.5–15-cm depth are identical. The resistance of DDT residues in the forest floor against downward transport by leaching, even at mean annual precipitation levels of 305 cm, is markedly evident in these data.

Mean annual precipitation (Table 4) is lower for each site along the Crater Lake transect relative to the three transects to the north. This transect also crosses the Cascade Range approximately 80 km south of any spray project conducted along the crest of the Cascades. The combined effect of these factors has resulted in a mean ΣDDT residue level (0.131 ppm) in the forest floor for this transect that is less than half the mean concentration for the other transects. Yet this residue level is considerably higher than the mean concentration of DDT in the forest floor of any of the transects across the Coast Ranges (Table 2). Aerial drift of DDT residues from the large spray projects conducted 80–322 km to the north has contributed to this level of contamination of unsprayed forests.

DDT ISOMERS AND METABOLITES

Residue levels of each isomer and metabolite of DDT in the forest floor and soil samples show essentially the same relationships and trends along transects of both mountain ranges except for TDE residues in samples from the Coast Ranges. Total residue levels were relatively low in samples from these transects, and the levels of TDE were too low to be quantified in more than half of the forest floor samples and in almost 75 percent of the soil samples from both depths. In contrast, residues of TDE could be easily quantified in over 75 percent of all samples from the Cascade Range.

TABLE 4. *Mean annual precipitation at each sampling site along transects across the Coast and Cascade Ranges in western Oregon, September–November, 1966* [1]

	Precipitation, cm				
	Distance from Coast, km				
Coast Range Transects	0	16	32	48	64
Wilson River	241	254	267	254	127
Yaquina	152	178	203	216	140
Umpqua	165	203	216	152	114
Rogue	203	229	267	216	203
	Elevation above Sea Level, Meters				
Cascade Range Transects	457	762	1067	1372	16 km E
Mt. Hood	190	203	216	229	127
Santiam Pass	267	279	305	190	89
Willamette Pass	114	152	165	165	76
Crater Lake	102	114	127	152	64

[1] Mean annual precipitation levels were estimated from U.S. Geological Survey isohyetal maps for western Oregon.

The largest proportion of all DDT residues found in samples from both sets of transects was present as *p,p'*-DDT. Residues of this isomer accounted for approximately 64 percent of the ΣDDT found in the forest floor (Table 5). The proportion of *p,p'*-DDT decreased with depth, whereas the relative amounts of *o,p'*-DDT and *p,p'*-DDE increased with depth. However, more than 80 percent of the total residues found at all sites remained in the forest floor. The relative proportions of the DDT isomers and metabolites, and the changes in relative distribution with sample depth, indicate that degradation is taking place slowly.

TABLE 5. *Mean residue levels of DDT isomers and metabolites in forest floors and soils of the Coast and Cascade Range transects expressed as a percentage of the mean ΣDDT residue level, September–November 1966*

Sample Depth, cm	*p,p'*-DDE	*o,p'*-DDT	*p,p'*-TDE	*p,p'*-DDT
COAST RANGE TRANSECTS				
Forest floor	14.93	21.35	—[1]	63.72
Soil: 0–7.5	22.38	27.31	—	50.31
Soil: 7.5–15	23.16	35.99	—	40.85
CASCADE RANGE TRANSECTS				
Forest floor	15.82	14.62	4.99	64.57
Soil: 0–7.5	19.70	26.34	4.33	49.63
Soil: 7.5–15	21.48	35.77	2.62	40.13

[1] TDE is not included because this metabolite could only be quantified in approximately 35 percent of the litter and soil samples from the Coast Range transects.

SIGNIFICANT EFFECTS OF TRANSECT, SITE, AND SAMPLING DEPTH

Residue data for each range were analyzed statistically to determine whether sampling transects or sampling

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sites (distance from coast or change in elevation) significantly influenced the level of DDT residue found. A split-split plot design was used, and the data were analyzed by analysis of variance. The first stage examined the influence of subsite and site over all three sampling depths, and the second stage provided a separate analysis for each depth. In addition, residue data for the Cascade Range were analyzed by a factorial analysis of variance using a randomized complete block design.

The average ΣDDT residue over all three sampling depths increased significantly with distance inland from the coast (Table 6). Average concentrations over all depths and for all four transects were 20.0, 20.9, 26.0, 29.6, and 46.9 ppm DDT for the sampling sites at 0, 16, 32, 48, and 64 km inland, respectively. Since these means represent 240 individual samples, this upward trend is not likely to be a chance occurrence. Sampling depth and the site × depth interaction were also highly significant ($P < 0.01$). These results were not unexpected since it was anticipated that if any measurable DDT residues were found, the highest concentrations would occur in the forest floor which represents the receiving surface for any atmospheric residues brought down by precipitation. The site × depth interaction indicates that the upward trend in residues with distance inland occurs at each depth, but the trend is less pronounced at each greater sampling depth.

TABLE 6. *Statistical analysis of the influence of transect, site, and subsite over all sampling depths on the distribution of total residues of DDT in the Coast Ranges, September–November 1966*

Source	DF	Sum of Sq.	Mean Sq.	F-value
Total	239	300,147		
Transects	3	160	53	n.s.
Site	4	22,888	5,722	16.16**
Error (a)	12	4,250	354	
Subsite	3	230	77	n.s.
Subsite × site	12	601	50	n.s.
Error (b)	36	3,955	110	
Depth	2	215,228	107,614	286.97**
Site × depth	8	32,723	4,090	10.91**
Subsite × depth	6	483	81	n.s.
Error (c)	24	9,006	375	
Error (d)	72	7,017	97	

NOTE: ** = Differences are highly significant ($P < 0.01$); n.s. = differences are not significant ($P > 0.05$).

Analysis for each depth did not provide any additional information. The influence of site showed the same highly significant increase with distance inland for forest floor residues. This relationship was only significant ($P < 0.05$) for residues in the surface layer of mineral soil, and nonsignificant ($P < 0.05$) for residue levels in the lower soil samples.

A similar series of analyses was conducted for each DDT isomer and metabolite. Residue levels of *p,p'*-DDE, *o,p'*-DDT, and *p,p'*-DDT showed the same relationships discussed above and the same levels of significance.

Residue data for the Cascade Range transects were statistically analyzed by the same split-split plot design (Table 7). There were no significant differences among average ΣDDT levels by transect or by sites for a given transect for either forest floor or soil. However, examination of the data presented in Table 3 indicates that residue levels are generally lower at each site located 16 km east of the crest of the Cascades, and that residue levels along the Crater Lake transect are lower than those observed for each of the three transects crossing the Cascade Range closer to the old spray projects. Residue data for the forest floor samples were analyzed by a factorial analysis of variance using a randomized complete block design. Residue levels in the forest floor were significantly lower east of the Cascades, and residues along the Crater Lake transect were significantly lower than residue levels in the forest floor samples from the other three transects (both at $P < 0.01$).

TABLE 7. *Statistical analysis of the influence of transect, site, and subsite over all sampling depths on the distribution of ΣDDT residues in samples from the Cascade Range, September–November 1966*

Source	DF	Sum of Sq.	Mean Sq.	F-value
Total	239	15,684,060		
Transects	3	542,593	180,864	1.81 n.s.
Site	4	517,790	129,448	1.29 n.s.
Error (a)	12	1,198,556	99,880	
Subsite	3	103,352	34,451	1.22 n.s.
Subsite × side	12	290,760	24,230	0.86 n.s.
Error (b)	36	1,012,599	28,128	
Depth	2	5,048,995	2,524,498	30.93**
Site × depth	8	922,449	115,306	4.69**
Subsite × depth	6	183,554	30,592	1.24 n.s.
Error (c)	24	1,958,987	81,624	
Error (d)	72	1,771,308	24,601	

NOTE: ** = Differences are highly significant ($P < 0.01$); n.s. = differences are not significant ($P > 0.05$).

This distribution of DDT residues in unsprayed areas is consistent with similar data reported by Cory et al. (*7*). In a study of the distribution of DDT residues in the Sierra Nevada Mountains, concentrations were markedly lower east of the crest. They also reported higher and more variable residue levels in samples from locations near old spray projects conducted in 1953 and 1956.

Closer examination of the data for each subsite along the Cascade Range transects shows that residue levels from all sampling sites and depths were extremely variable. The standard deviation of the mean for ΣDDT residues in the forest floor samples from the Santiam transect is greater than the mean. The causes of this variation are most likely the relative position of the sampling sites in reference to the location of the old

spray projects and the prevailing climatic conditions at the time those 1.16 million hectares were sprayed with DDT. The one sampling site that unintentionally fell in an old spray unit greatly distorts the residue levels for that site and for the transect, but it does not account for all variation observed among and between sampling sites. This discussion applies equally to all statistical analyses conducted on the Cascade Range residue data for each depth and for each DDT isomer and metabolite.

Conclusions

The primary purposes of this study were to determine to what extent untreated forested areas in western Oregon may have become contaminated through washout of DDT residues known to be present in the atmosphere, and to establish background levels of DDT residues in forest litter and soil. Perhaps the most important result obtained is the fact that measurable quantities of DDT were found at every site sampled along each of the eight transects. Residue levels along transects across the Coast Ranges increased significantly with distance inland from the coast. This trend is readily explained in that each transect ends in a forested area adjacent to agriculturally important inland valleys or population centers which serve as a source of the pesticide residues. Residue levels along transects across the Cascade Range were considerably higher than those found in the Coast Ranges because of the influence of a number of large insect control projects conducted along the crest of the Cascades between 1949 and 1953. Distance and direction of sampling sites from these sprayed areas have produced a wide variation in residue levels which tends to mask the influence of annual rainfall distribution and other local differences in topography.

Although DDT residues were found at every point sampled, the levels of these residues were generally low. Maximum concentrations of DDT in forest floor samples from the Coast Ranges did not exceed 0.17 ppm. Residue levels in forest floor samples from the Cascade transects were generally three to five times higher than those from Coast Ranges, but mean residues still did not exceed 0.50 ppm DDT. Low levels in the surface mineral soils of both sets of transects further substantiate the fact that DDT is not readily leached into forest soils. The tenacity with which the organic horizons of forest soils hold residues of DDT strongly suggests that the levels of residue measured are not likely to become available to nontarget organisms in toxic amounts (*28*).

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FISH, WILDLIFE, AND ESTUARIES

Influence of a Local Source of DDT Pollution on Statewide DDT Residues in Waterfowl Wings, Northern Alabama, 1978–79

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ABSTRACT

Heavy DDT contamination resulting from a former DDT manufacturing plant in northern Alabama has influenced statewide averages of DDT, DDE, and TDE residues in duck wings tested in the National Pesticide Monitoring Program. In states where contaminant levels in duck wings are high, residue analyses of wings categorized by finer geographic subdivision may be useful in defining the areas of heaviest contamination.

Introduction

The Fish and Wildlife Service, U.S. Department of the Interior, began nationwide monitoring of organochlorine residues in the wings of black ducks (*Anas rubripes*) and mallards (*Anas platyrhynchos*) in 1965 as part of the National Pesticide Monitoring Program (*1*). Waterfowl wings submitted to the Fish and Wildlife Service annual Waterfowl Harvest Survey were analyzed for organochlorine residues for the years 1965–67 (*1*), 1969–70 (*2*), 1972–73 (*5*), and 1976–77 (*6*). Analyses were based on sample pools of 25 wings each with the number of pools from each state varying in proportion to the number of wings submitted from each state. Although organochlorine residues in duck wings are reported for individual states, waterfowl are migratory, and it is conceivable that these residues may not accurately reflect the relative degrees of contamination between states. However, consistent outstanding trends in residue data over several collection periods indicate that local organochlorine contamination may be recognizable by monitoring residues in duck wings.

Duck wings from Alabama consistently have shown elevated concentrations of DDT and its metabolites, in comparison to other states. Therefore, duck wings from Alabama would appear to be prime candidates for determining the usefulness of this type of monitoring in pinpointing local sources of organochlorine contamination. Alabama and California were the only states in which DDE in mallard wings exceeded 1 ppm for at least three of the five previous sampling periods. Mallard wings from Alabama had the highest average DDE residues of all states in the 1965–66 and 1969–70 surveys (*1*, *2*). In 1972, duck wings from Alabama had higher DDT and DDE residues than any other state (*5*), exceeding national averages by factors of 12.9 and 6.2, respectively. In 1976, Alabama was highest for DDT and third highest for DDE, at 3.2 and 2.6 times the national averages (*6*).

It seems likely that the high DDT and DDE concentrations observed in duck wings from Alabama were due largely to industrial contamination of their winter habitat. From 1949 to 1970, a commercial DDT manufacturing plant released its effluent into Huntsville Spring Branch, a tributary of the Tennessee River in northern Alabama. DDT and its metabolites in sediments of a 4-mile portion of Huntsville Spring Branch have been estimated at 4,000 tons (Tennessee Valley Authority, unpublished report, 1978). This heavily contaminated area and the area immediately downstream from this site are encompassed by the Wheeler National Wildlife Refuge, a major waterfowl wintering area in Alabama. The present study examines the influence of this point source of pollution on statewide averages of DDT, DDE, and TDE concentrations in duck wings. Also, the authors explore the usefulness of subclassifying duck wings by county of collection, for the purpose of identifying local sources of organochlorine pollution.

Sampling and Analysis

Mallard wings from Alabama were collected during the 1978–79 Waterfowl Harvest Survey, the same source

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of wings used for the National Pesticide Monitoring Program. Wings were sorted by county of collection and subdivided by age-sex groups. Wings sorted in this fashion were then randomly assigned to composite samples or pools of five wings each. Wings from adjacent counties were pooled in some instances to provide enough wings for analysis. Remaining wings were then combined into a northern Alabama pool or a southern Alabama pool. A total of 44 wing pools was analyzed.

Wings were shipped to Raltech Scientific Services, Inc., Madison, Wisconsin, for residue analyses. They were prepared and analyzed by the same procedure established for the Nationwide Pesticide Monitoring Program (*6*), except that the cleanup solvent was a mixture of 15 percent dichloromethane and 85 percent cyclohexane. The lower limit of quantification of DDT and its metabolites was 0.01 ppm. Percent recoveries for spiked samples were 75 for DDT, 93 for DDE, and 80 for TDE. Data were not corrected for percent recoveries.

Results and Discussion

ΣDDT in duck wings from Alabama varied considerably by region and was highest in counties near the DDT manufacturing plant (Table 1, Fig. 1). Pools of wings from Limestone and Madison Counties had ΣDDT residues that averaged 10.8 and 18 times higher, respectively, than the combined average of all other counties or county groups ($P < 0.05$). Heaviest contamination appeared to be localized in these two counties; residues in adjoining counties were not greatly elevated (Fig. 1). The former DDT manufacturing site is in Madison County, 15 km east of Limestone County. Wheeler National Wildlife Refuge is located in Madison, Limestone, and Morgan Counties. Pollution from the DDT plant therefore seems to be the likely source of the high ΣDDT concentrations in waterfowl from Madison and Limestone Counties. Waterfowl banding records show that mallards harvested in Madison and Limestone Counties are not members of a nesting population that is distinct from that of the rest of the state. Therefore, the common link for contaminated birds is their wintering area and not their breeding grounds.

The high mean concentrations of DDT, DDE, and TDE observed in duck wings from Alabama during previous monitoring studies (*1, 2, 4, 6*) have undoubtedly been strongly influenced by this localized contamination; a large proportion of the total number of mallard wings from Alabama was submitted from the northern quarter of the state and 5–35 percent came from Limestone and Madison Counties (Table 2). Limestone, Madison, and Morgan Counties accounted for 27–50 percent of the wings submitted during each of the sampling years. The highest residue concentrations during the five sampling periods of the National Pesticide Monitoring Program (Table 3) occurred when the greatest proportion of wings was harvested in areas in northern Alabama (Table 2).

The lowest statewide residues of ΣDDT occurred when the proportion of wings from Madison and Limestone Counties was lowest. Otherwise there are no apparent simple correlations between specific residue means and proportions of the harvest taken from various areas in northern Alabama. This lack of correlation is undoubtedly due to the small number of pools analyzed each year and the high variation between pools (Table 3). Such variation may be caused by very high residues in a few individuals of a sample pool. For example, if 24 wings in a pool contained 1 ppm ΣDDT and a single wing contained 101 ppm ΣDDT, then the sample pool residue would be 5 ppm. Authors have previously reported residues of up to 480 ppm ΣDDT in mallard carcasses from Huntsville Spring Branch (*4*); therefore, it is likely that extremely high residues in a few wings would contribute materially to the great variation seen in past monitoring studies (Table 3).

The distribution of mallards and black ducks and the proportion of ducks harvested in different localities within a state determine the effectiveness of using organochlorine residues in duck wings to pinpoint polluted environments. States where organochlorine residues in waterfowl wings are above the national average may have waterfowl harvests occurring in contaminated environments. Thus residue analyses of duck wings might be useful in pinpointing local areas of contamination if areas of wing collection are defined by subclassification below the state level. Authors conclude from the present study that the use of duck wings to locate areas of contamination within a state show the greatest promise when residues in composite sample pools from various states are known to be much higher than national averages.

Finally, comparison of the present data with those of experimental studies of black ducks fed DDE (*3*) indicates that the local DDT contamination detected by the present study in Alabama may have serious implications for the reproductive health of waterfowl wintering in this area. Longcore and Stendell (*3*) provided data suggesting that DDE residues of 2–3 ppm in wings can be correlated with eggshell thinning and decreased productivity in female black ducks. DDE residue concentrations exceeded 3 ppm in 6 of 15 pools from Limestone County; in one pool it reached 10 ppm (Tabe 1) but concentrations of DDE may have been slightly overestimated compared to those reported by Longcore and Stendell (*3*) because of possible differences in moisture loss. Although residues in female mallards from Limestone and Madison Counties were less than for males, fewer pools of wings from females

TABLE 1. *DDT, DDE, and TDE residues in pools of mallard wings from Alabama, 1978–79 hunting season* [1]

Designation [2]	County	Statistic	Residues, ppm Wet Weight											
			Immature Females			Immature Males			Adult Females			Adult Males		
			DDE	DDT	TDE	DDE	DDT	TDE	DDE	DDT	TDE	DDE	DDT	TDE
1	Lauderdale, Colbert, Lawrence	Mean±SD	0.32	0.02	0.02	—	—	—	0.31	ND	ND	—	—	—
		Range	—	—	—	—	—	—	—	—	—	—	—	—
		N	1	1	1	—	—	—	1	1	1	—	—	—
2	Limestone	Mean±SD	0.76±0.50	0.03±0.01	0.16±0.20	0.87±1.20	0.05±0.08	0.12±0.17	0.02	ND	ND	4.40±5.10	0.90±0.75	1.80±0.47
		Range	0.40–1.10	0.02–0.04	0.01–0.31	0.16–2.70	0.01–0.17	0.02–0.38	—	—	—	0.11–10.0	0.37–1.40	1.50–2.10
		N	2	2	2	4	4	4	1	1	1	3	3	3
3	Madison	Mean±SD	2.60±3.20	0.21±0.29	0.62±0.71	1.40±0.52	2.70±2.60	0.74±0.98	—	—	—	5.61	0.07	0.41
		Range	0.37–4.80	0.00–0.41	0.12–1.12	1.00–1.70	0.79–4.50	0.04–1.40	—	—	—	—	—	—
		N	2	2	2	2	2	2	—	—	—	1	1	1
4	Jackson, Marshall, Morgan	Mean±SD	0.49	0.03	0.00	—	—	—	0.21	0.09	0.03	0.26±0.06	0.15±0.02	0.03±0.03
		Range	—	—	—	—	—	—	—	—	—	0.21–0.33	0.00–0.03	0.01–0.05
		N	1	1	1	—	—	—	1	1	1	2	2	2
5	Green, Sumter, Choctaw	Mean±SD	—	—	—	0.44±0.44	0.03±0.04	0.01±0.01	—	—	—	—	—	—
		Range	—	—	—	0.13–0.75	0.00–0.06	0.00–0.01	—	—	—	—	—	—
		N	—	—	—	2	2	2	—	—	—	—	—	—
6	Clarke, Wilcox, Washington	Mean±SD	0.03	0.00	0.00	0.02	0.00	0.00	0.07	0.00	0.00	0.16±0.02	0.01±0.01	0.00
		Range	—	—	—	—	—	—	—	—	—	0.14–0.17	0.00–0.01	0.00–0.00
		N	1	1	1	1	1	1	1	1	1	2	2	2
7	Mobile, Baldwin	Mean±SD	—	—	—	0.06	0.00	0.00	—	—	—	0.18	0.01	0.00
		Range	—	—	—	—	—	—	—	—	—	—	—	—
		N	—	—	—	1	1	1	—	—	—	1	1	1
	Northern County Pool	Mean±SD	0.25	0.45	0.11	0.80±0.82	0.35±0.46	0.12±0.12	0.61±0.74	0.06±0.07	0.02±0.02	—	—	—
		Range	—	—	—	0.23–1.70	0.02–0.87	0.03–0.24	0.09–1.13	0.01–0.11	0.00–0.03	—	—	—
		N	1	1	1	3	3	3	2	2	2	—	—	—
	Southern County Pool	Mean±SD	0.08±0.02	0.00	0.00	—	—	—	0.07	0.00	0.00	—	—	—
		Range	0.06–0.09	0.00–0.00	0.00–0.00	—	—	—	—	—	—	—	—	—
		N	2	2	2	—	—	—	1	1	1	—	—	—
	Controls [3]	Mean±SD	0.05±0.04	0.01±0.01	0.01±0.01									
		Range	0.01–0.11	0.00–0.02	0.00–0.03									
		N	5	5	5									

NOTE: SD = standard deviation; ND = not detected.

[1] Each pool consisted of five wings.

[2] See Figure 1.

[3] Control wing pools consisted of wings from five juveniles, without regard to sex. Wing were obtained from pen-raised mallards.

were sampled. Authors have found carcass residues of 480 ppm ΣDDT in female mallards from Wheeler National Wildlife Refuge (*4*), indicating that females also may have high ΣDDT residues.

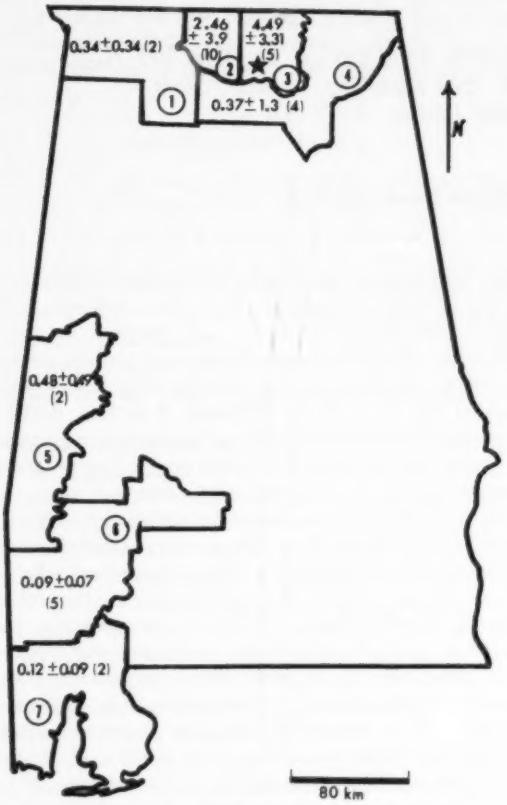

FIGURE 1. *ΣDDT residues in mallard wings from Alabama, 1978–79. Mean ± 1 standard deviation in ppm wet weight for pools of five wings. Number of pools are indicated in parentheses; encircled numbers refer to the county key in Table 1. Star shows location of former DDT manufacturing plant.*

Acknowledgments

The idea for this study originated through discussions with F. X. Lueth, retired, Alabama Department of Conservation. Wings were obtained through the cooperation of S. M. Carney, Waterfowl Harvest Surveys, Fish and Wildlife Service, U.S. Department of the Interior. E. H. Dustman and B. W. Cain offered advice on manuscript preparation.

TABLE 2. *Number of mallard wings submitted from selected areas in Alabama during five years of the National Pesticide Monitoring Program, 1965–76*

Area	Year									
	1965		1966		1969		1972		1976	
	N	%[1]	N	%	N	%	N	%	N	%
Madison and Limestone Counties	27	17	96	35	3	5	60	29	126	23
Madison, Limestone and Morgan Counties	54	34	137	50	16	28	67	33	108	27
Northern quarter of state	100	64	193	71	29	51	140	69	307	67
Entire state	157	100	271	100	57	100	202	100	460	100

[1] Percentage of the total number of wings submitted from Alabama for the year indicated.

TABLE 3. *DDE, DDT, and TDE residues in composite samples of mallard wings from Alabama for the first five years of the National Pesticide Monitoring Program, 1965–76* [1]

Chemical	Statistic	Year				
		1965	1966	1969	1972	1976
DDE	Mean ± SD	0.76	2.62	1.75	1.85 ± 1.53	0.69 ± 0.34
	Range	0.43–5.31 [2]		—	0.79–4.12	0.17–2.39
	N	5	6	1	4	6
DDT	Mean ± SD	0.30	0.35	0.09	1.03 ± 1.31	0.19 ± 0.06
	Range	—	—	—	0.23–2.98	0.01–0.41
	N	5	6	1	4	5
TDE	Mean ± SD	0.11	0.56	2.07	0.44 ± 0.53	0.38 ± 0.33
	Range	—	—	—	0.09–1.23	<0.01–1.72
	N	5	6	1	4	5

[1] Each composite sample consisted of 25 wings.
[2] Range for 1965 and 1966 data combined.

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Organochlorine Residues and Shell Thicknesses in Eggs of the Clapper Rail, Common Gallinule, Purple Gallinule, and Limpkin (Class Aves), Eastern and Southern United States, 1972–74

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ABSTRACT

Organochlorine residues and shell thicknesses were surveyed in eggs of the clapper rail (Rallus longirostris), *purple gallinule* (Porphyrula martinica), *common gallinule* (Gallinula chloropas), *and limpkin* (Aramus guarauna) *from the eastern and southern United States. Clapper rail eggs were collected during 1972–73 in New Jersey, Virginia, and South Carolina. During 1973–74, gallinule eggs were collected in Florida, South Carolina, and Louisiana, and limpkin eggs were collected in Florida. Egg contents were analyzed for residues of organochlorine pesticides, including DDT, TDE, DDE, dieldrin, mirex, heptachlor epoxide, oxychlordane,* cis-*chlordane (and/or* trans-*nonachlor),* cis-*nonachlor, hexachlorobenzene (HCB), toxaphene, and endrin, and for polychlorinated biphenyls (PCBs). Shell thicknesses of recent eggs of these species were compared with archival eggs that had been collected before 1947. With the exception of the limpkin, the majority of eggs analyzed contained residues of* p,p'-*DDE and PCBs. Geometric means ranged from 0.10 ppm to 1.3 ppm. Small amounts (<1.0 ppm) of mirex, dieldrin,, cis-chlordane (and/or* trans-*nonachlor), TDE, and DDT were detected in a few eggs. No evidence of eggshell thinning was found for any of the species studied. DDE residues in clapper rail eggs were higher in New Jersey and Virginia than in South Carolina.*

Introduction

Organochlorine compounds are well known as persistent environmental contaminants that tend to accumulate in the upper trophic levels of food chains. The occurrence of organochlorine residues in tissues of carnivorous animals and the effects of these contaminants on their reproduction, behavior, and survival has been extensively documented (*14, 16*). However, residues in animals at intermediate levels of food chains are less well known.

Authors report here the results of a survey of residues and shell thicknesses in eggs of four species of the avian order Gruiformes: the clapper rail (*Rallus longirostris*), purple gallinule (*Porphyrula martinica*), common gallinule (*Gallinulla chloropas*), and limpkin (*Aramus guarauna*). Environmental contaminants in these species are of interest because they occupy intermediate positions in the food chains of North American wetland ecosystems, and because rails and gallinules are hunted as game and consumed by humans in many areas. Several species or subspecies of Gruiformes have also been designated as endangered, including the whooping crane (*Grus americana*), Mississippi sandhill crane (*Grus canadensis pulla*), California clapper rail (*Rallus longirostris obsoletus*), light-footed clapper rail (*R. l. levipes*), Yuma clapper rail (*R. l. yumanensis*), and Hawaiian gallinule (*Gallinula chloropus sandvicensis*) (*17*). Moreover, the limpkin, whose distribution in the United States is limited to Florida, has been designated by that state as endangered. It feeds almost exclusively on large freshwater snails, mainly the apple snail (*Pomacea paludosa*) (*12*). This snail is considered also to be the sole source of food for the endangered Everglade kite (*Rostrhamaus sociabilis*) (*3*).

Small amounts of dieldrin (<0.04 ppm), *p,p'*-DDT (<0.06 ppm), *p,p'*-TDE (<0.02–0.59 ppm), and *p,p'*-DDE (0.06–0.20 ppm), have been reported in tissues of the endangered whooping crane (*11*), but eggshell thickness has remained normal in this species (*2*). Notably high levels of dieldrin were found in eggs of purple gallinule and common gallinule collected from rice fields in Louisiana (*5, 9*). However, egg hatchability, chick survival, and eggshell thickness for gallinules nesting in rice fields did not differ significantly from gallinules nesting in marsh areas where residue levels were much lower.

Flickinger and King (*7*) reported 20.0 ppm and 5.5 ppm dieldrin and 21.0 ppm and 1.2 ppm DDT and metabolites in carcasses of two king rails (*Rallus elegans*) in Texas. The carcass of a common gallinule collected in the same area contained only 0.1 ppm ΣDDT and <0.1 ppm dieldrin. Residue levels in one of the king rails

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were among the highest and those in the gallinule were among the lowest reported in 62 specimens of birds representing 32 species found dead near aldrin-treated rice fields during 1967–71. Foehrenbach et al. (*8*) reported a mean of 0.38 ppm DDT and metabolites in four clapper rail eggs from Long Island, New York. Authors know of no other published data on organochlorine residues and eggshell thickness among gruiform birds.

Sampling and Analysis

Clapper rail eggs were collected during 1972–73 from Cape May and Atlantic Counties, New Jersey; Accomack and Northampton Counties, Virginia; and Charleston County, South Carolina. Gallinule eggs were collected during 1972–73 from Brevard, Glades, Lee, and Marion Counties, Florida; Beaufort County, South Carolina; and Cameron Parish, Louisiana. Limpkin eggs were collected during 1973–74 from the northwest side of Lake Okeechobee, Glades County, Florida.

Complete clutches and addled eggs were collected; two eggs from each clutch were wrapped in aluminum foil and placed in plastic containers to retard moisture loss. Eggs were refrigerated until the contents were removed, placed into chemically cleaned jars, and frozen pending chemical analysis. Only one egg per clutch was analyzed, but shells of all eggs were saved for comparisons of shell thickness. Egg volumes were measured to the nearest 1.0 ml by water displacement before the contents were removed. This allowed residues to be adjusted to fresh wet weight, assuming specific gravity of 1.0 as suggested by Stickel et al. (*15*).

Egg contents were homogenized in a mixer, and a 10-g aliquot was blended with sodium sulfate and extracted 7–8 hours with hexane in a Soxhlet apparatus. Cleanup of the extract, and separation and quantitation of organochlorines were similar to the procedures used for the analysis of eagle carcasses (*6*). In summary, the concentrated hexane extract was placed on a Florisil column and eluted with 200 ml of 6 percent ethyl ether in hexane to remove lipids. The Florisil eluate was concentrated and eluted from a silicic acid column to separate pesticides from polychlorinated biphenyls (PCBs). The organochlorines separated into three silicic acid eluates were identified and quantitated by electron-capture gas chromatography on a 1.83-m glass column packed with a mixture of 4 percent SE-30 and 6 percent QF-1 on 100–120-mesh Supelcoport. Pesticides were quantitated with a computing integrator; PCBs were quantitated by comparing total peak area with that of Aroclor 1254 or 1260, whichever most closely resembled the gas chromatographic profile of the sample. Residues in about 10 percent of the samples were confirmed by gas chromatography-mass spectrometry.

Samples were analyzed for DDT, TDE, DDE, dieldrin, mirex, heptachlor epoxide, oxychlordane, *cis*-chlordane (and/or *trans*-nonachlor), *cis*-nonachlor, hexachlorobenzene (HCB), toxaphene, endrin, and PCBs.

Recoveries of pesticides and PCBs from spiked egg tissue ranged from 83 percent to 104 percent. Residues in the present report were not adjusted on the basis of these recoveries. Sensitivity of detection was 0.1 ppm for pesticides and 0.5 ppm for PCBs. When PCBs were detected in trace amounts (<0.5 ppm), they were considered as 0.25 ppm for purposes of this report. Chemical residue values were transformed to their common logarithms for statistical analysis. A unit of 1.0 was added to each value prior to transformation, to accommodate zero values. Total lipids averaged 8.7 percent in clapper rail eggs, 8.8 percent in limpkin, 10.2 percent in purple gallinule, and 10.4 percent in common gallinule.

For studies of shell thickness, the eggs collected for residue analyses were supplemented by eggs from museum collections. Authors compared shell thicknesses of egg collected since 1946 with shell thicknesses of eggs collected before the widespread use of organochlorine pesticides. Shell thickness was measured to the nearest 0.01 mm with a modified Starrett micrometer after the shells had dried at room temperature for at least one month. Three measurements were taken at the equator of each egg and included the shell and shell membranes. Measurements were averaged to yield a single value for each egg in the clutch, and values for all eggs in a clutch were averaged to yield a clutch mean thickness, the basic unit of measurement for statistical treatment.

For each species, eggshell thickness data for various geographic localities were grouped into time periods pre-1947 and 1947–74. Variations among localities and time periods were subjected to two-way, nonrandom analysis of variance (ANOVA). Statistical testing of differences in mean thicknesses between time periods and geographic locations followed the procedures of Sokal and Rohlf (*13*).

Results and Discussion

CLAPPER RAIL

All 49 eggs analyzed contained *p,p'*-DDE, but mean residue levels were relatively low (Table 1). A mean value of 1.3 ppm in New Jersey eggs was more than three times as high as the mean for eggs from South Carolina. Mean residue levels for Virginia and New Jersey eggs are not significantly different but both are significantly higher than the mean for South Carolina eggs ($P < 0.05$, ANOVA, log-transformed data). Residues of PCBs occurred in 100 percent of the samples

TABLE 1. *DDE and PCB residues in eggs of the clapper rail, purple gallinule, common gallinule, and limpkin from eastern United States, 1972–73*

Locality	Organochlorine	n [1]	PPM, Wet Wt: Geom. Mean	Median	Range	Number with Residues
CLAPPER RAIL						
South Carolina	DDE	10	0.41	0.52	0.10–1.1	10
	PCB	10	<0.5	<0.5	ND–1.2	6
Virginia	DDE	19	0.97	1.0	0.31–2.6	19
	PCB	19	<0.5	<0.5	ND–2.1	16
New Jersey	DDE	20	1.3	1.2	0.47–6.4	20
	PCB	20	<0.5	<0.5	<0.5 –2.7	20
PURPLE GALLINULE						
Florida	DDE	10	0.18	0.13	ND–0.95	6
South Carolina	DDE	1	0.29	—	—	1
COMMON GALLINULE						
Florida	DDE	15	0.21	0.13	ND–0.80	11
Louisiana	DDE	9	<0.10	0.0	ND–0.10	2
South Carolina	DDE	1	0.24	—	—	1
LIMPKIN						
Florida	DDE	14	0.18	0.0	ND–5.6	4

NOTE: ND = not detected.
[1] Number of clutches represented.

from New Jersey, 84 percent from Virginia, and 60 percent from South Carolina. Mean values for PCBs were < 0.5 ppm for all three localities.

No organochlorine residues other than DDE and PCBs were detected in eggs from South Carolina. Mirex (0.83 ppm) was found in one egg from Accomack County, Virginia, and 0.09 ppm dieldrin and a trace of *trans*-nonachlor were found in another egg from that locality. In New Jersey samples, trace amounts (< 0.10 ppm) of *trans*-nonachlor occurred in nine eggs; mirex was detected in five eggs (mean = 0.34 ppm; range 0.16–0.45 ppm); TDE in three eggs (mean = 0.30 ppm; range 0.20–0.35 ppm); and DDT in one egg (0.25 ppm). Heptachlor epoxide, oxychlordane, *cis*-nonachlor, HCB, toxaphene, and endrin were not detected in any clapper rail eggs analyzed.

Although authors were unable to collect recent samples of clapper rail eggs from Florida for residue analysis, nine clutches (six from the west coast and three from the east coast of Florida) that had been collected after 1946 were present in museum collections. These nine clutches were used in the present comparisons of mean eggshell thicknesses (Table 2).

Within each locality, there were no significant differences ($P > 0.05$ ANOVA) between mean eggshell thicknesses for the two selected time periods (Table 2). However, significant differences ($P < 0.05$) did occur in shell thicknesses between geographic localities; eggshells from Virginia and New Jersey were thicker than those from the southern states. These observed geographic differences probably reflect

TABLE 2. *Variations in shell thicknesses of clapper rail eggs from eastern United States, 1863–1973*

Locality	1863–1946: n [1]	Mean Th, mm [2]	1947–1973: n	Mean Th, mm	% Change	1863–1973: n	Combined Mean Th, mm [2]
Florida (west)	38	0.241	3	0.242	0	41	0.241 A
Florida (east)	55	0.244	6	0.257	+5	61	0.245 A
Georgia, Carolinas	63	0.241	7	0.247	+2	70	0.242 A
Virginia	57	0.258	22	0.262	+2	79	0.259 B
New Jersey	25	0.260	18	0.255	−2	43	0.258 B

NOTE: No significant differences (ANOVA, $P > 0.05$) were detected between pre-1947 and recent eggs.
[1] n = Number of complete clutches.
[2] Means for each locality calculated from clutch mean thickness. Estimated variance (S^2) = 0.000282602 with 274 degrees of freedom.
[3] Among localities, combined means which are not significantly different share common letters (SNK test, $P > 0.05$).

environmental differences in the localities or genetic differences between species which inhabit these areas. Virginia and New Jersey are within the range of the northern clapper rail (*R. l. crepitans*). Localities in Georgia, North Carolina, South Carolina, and the east coast of Florida are within the range of the Wayne clapper rail (*R. l. waynei*). The west coast of Florida is occupied by the Florida clapper rail (*R. l. scottii*) (*1*). Accordingly, the northern clapper rail has thicker eggshells than the other two subspecies. Even with these relatively large numbers of eggs from museum collections, the authors lacked samples for many individual years and localities, especially the period from 1940 to 1971 and years prior to 1895. Authors attempted to examine variation in eggshell thicknesses among time periods of shorter duration than those given in Table 2, but results were inconclusive because gaps in the data precluded statistical testing.

Clutch sizes in clapper rails averaged 8.5 eggs (range 5–13) for 237 clutches of pre-1947 eggs and 8.6 (range 5–13) for 56 clutches of recent eggs.

No significant correlations were found between shell thickness and DDE ($r = -0.08$) or PCBs ($r = 0.04$), but a significant correlation was detected between DDE and PCBs ($r = 0.38$, $P < 0.01$).

L. J. Blus (Patuxent Wildlife Research Center, personal communication, 1975) collected seven clapper rail eggs, one from each of seven nests, from Charleston County, South Carolina in 1971. DDE in these eggs averaged 1.53 ppm (geometric mean; unpublished data). The difference in mean DDE residues between 1971 and 1972 (Table 1) is significant ($P < 0.05$) and the decline is consistent with observed declines in DDE residues in eggs of brown pelicans (*Pelecanus occidentalis*) from the same locality during 1969–73 (*4*). Sharp declines in DDE residues in clapper rail tissues and other aquatic fauna from New Jersey have also been reported (*10*).

PURPLE GALLINULE

DDE was the only organochlorine residue detected in eggs of purple gallinules, and levels were low (Table 1). A series of 89 clutches of eggs collected in Florida between 1885 and 1940 averaged 0.218 mm in thickness, and 15 clutches collected in 1948, 1962, and 1973 averaged 0.213 mm. The difference between clutches collected pre-1947 and post-1947 is not significant ($P > 0.05$). Authors had insufficient samples of recent eggs of this species from other localities to compare their shell thicknesses. However, 45 clutches of pre-1947 eggs from South Carolina had a mean thickness of 0.210 mm, and 13 clutches from Louisiana averaged 0.214 mm. Clutch sizes in the purple gallinule averaged 6.0 eggs (range 4–10) for 147 clutches of pre-1947 eggs and 5.9 (range 4–9) among 15 clutches of recent eggs.

COMMON GALLINULE

DDE was the only organochlorine residue detected in eggs of the common gallinule with the exception of one egg from South Carolina which contained 0.12 ppm mirex. Incidence of occurrence and mean residue levels were obviously lower in Louisiana than in Florida (Table 1).

Sufficient samples of recent eggs were available for comparison of shell thicknesses from only three regions (Table 3). Mean differences between time periods were not significant ($P > 0.05$) for any of the three areas. However, geographic differences in mean thickness did occur (Table 3). The pattern of differences is similar to that for the clapper rail: eggs from the southern states have thinner shells than those from the northeast. However, common gallinules have not been differentiated into more than one subspecies in the United States.

TABLE 3. *Variation in shell thickness of common gallinule eggs from eastern United States, 1884–1973*

	1884–1946		1947–1973			1884–1973
States	n [1]	Mean Th, mm [2]	n	Mean Th, mm	% Change	n	Combined Mean Th, mm [3]
Georgia, South Carolina	17	0.268	4	0.275	+2	21	0.269 A
Florida	39	0.276	23	0.281	+2	62	0.278 B
Illinois, Iowa, Wisconsin	27	0.280	0	—	—	27	0.280 ABC
Louisiana, Texas	4	0.284	9	0.287	+1	13	0.286 BCD
Ohio, Michigan	29	0.288	0	—	—	29	0.288 CD
Massachusetts, New Jersey, New York, Virginia, Pennsylvania [4]	57	0.294	0	—	—	57	0.294 D

NOTE: No significant differences (ANOVA, $P > 0.05$) were detected between pre-1947 and recent eggs.

[1] n = Number of clutches.

[2] Thickness means for each locality calculated from clutch mean thickness. Estimated variance (S^2) = 0.000313214 with 199 degrees of freedom (ANOVA).

[3] Among localities, combined means which are not significantly different share common letters (SNK test, $P > 0.05$).

[4] Forty-eight clutches were from Pennsylvania and New Jersey.

Clutch sizes in the common gallinule averaged 7.8 eggs (range 4–14) for 173 clutches of pre-1947 eggs and 6.7 (range 5–9) among 36 clutches of recent eggs.

LIMPKIN

DDE was detected in only four of 14 clutches of limpkin eggs, and no other organochlorine residues were found in any eggs. One of the four eggs contained 5.6 ppm DDE, but the other three contained 0.23, 0.14, and 0.12 ppm. These low residues are consistent with reported low residues of DDE in apple snails (9).

A series of 124 clutches of limpkin eggs collected in Florida between 1882 and 1946 averaged 0.360 mm in thickness; in 151 clutches collected after 1947, shell thickness averaged 0.357 mm. The difference in means is not significant ($P > 0.05$). Of the 151 recent clutches, 100 were collected during 1950 in Dade and Indian River Counties and averaged 0.357 mm. Using analysis-of-variance procedures, no significant differences in shell thickness means were detected in comparisons of limpkin eggs on a yearly or decade basis, and no differences in thickness were found among eggs in different stages of incubation, among eggs of various clutch sizes, or among complete and incomplete clutches.

Clutch sizes of the limpkin averaged 5.5 eggs (range 3–7) for 124 clutches of pre-1947 eggs and 5.3 (range 3–7) among 151 recent clutches.

Conclusions

Eggs of clapper rail, common gallinule, purple gallinule, and limpkin (representing 139 clutches collected in the eastern United States during the early 1970s), contained low residues of DDE and PCBs, with geometric means ranging from <0.10 ppm to 1.3 ppm. Small amounts (<1.0 ppm) of mirex, dieldrin, *cis*-chlordane (and/or *trans*-nonachlor), TDE, and DDT were detected in a few eggs. Heptachlor epoxide, oxychlordane, *cis*-nonachlor, HCB, toxaphene, and endrin were not detected. No changes in eggshell thickness between time periods were evident in any of the four species. Geographic differences in thickness means were found in eggs of clapper rail and common gallinule.

Acknowledgments

We thank L. J. Blus in South Carolina, Rod Chandler in Florida, F. A. Ferrigno, Sr. and Lee Widjeskog in New Jersey, and S. R. Aycock in Louisiana for assistance in collecting recent eggs. We acknowledge the cooperation of curatorial personnel in the following museums where oological collections were examined: American Museum of Natural History, Carnegie Museum, Charleston (S.C.) Museum, Clemson University, Delaware Museum of Natural History, Florida

State Museum, Louisiana State University, Museum of Comparative Zoology (Harvard), Ohio State University, Peabody Museum of Natural History (Yale University), Philadelphia Academy of Sciences, University of Massachusetts, and U.S. National Museum.

K. P. Burnham, D. E. Coyne, and F. R. Fieher wrote or modified computer programs and provided useful suggestions relative to statistical treatment and interpretation of data.

We appreciate critical reviews of the manuscript by A. S. Federighi, D. H. White, and S. A. Wiemeyer.

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Mercury Levels in Waterfowl from Manitoba, Canada, 1971–72

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ABSTRACT

From two locations in Manitoba suspected of mercury pollution, waterfowl were collected during 1971 and 1972 to determine the incidence and nature of the contamination. Total mercury concentrations averaged 0.18 ppm and 0.22 ppm in breast muscle of 169 adult dabbling (Anatini) *and 77 adult diving ducks* (Aythyini, Mergini, *and* Oxyurini), *respectively. Mercury concentrations in breast muscles of immature ducks of these tribes averaged 0.15 ppm total mercury for 70 dabblers and 0.16 ppm for 40 divers. Mean mercury residues in livers were 0.54 ppm and 0.31 ppm, respectively, in 60 adults and 30 immature dabblers and 0.93 ppm and 0.29 ppm, respectively, in 31 adults and 15 immature divers. Primary feathers of 20 adult and 12 immature dabblers collected in the Saskatchewan River Delta averaged 2.67 ppm and 1.34 ppm, while 10 adult and 7 immature divers averaged 1.48 ppm and 1.11 ppm, respectively. Only in 20 ducks, 10 dabblers and 10 divers, did mercury concentrations in the breast muscle exceed 0.50 ppm. Statistically significant relationships for the concentration of mercury in feathers to breast muscle, feathers to liver, and breast muscle to liver were found for spring adults and for immature dabbling ducks. The only significant relationship for divers was feather to liver concentrations for immature ducks and breast muscle to liver concentrations of spring adults in 1972 in the Saskatchewan River Delta.*

Introduction

In 1970, Fimreite (*5*) predicted that industrial, domestic, and natural sources of mercury had the potential to seriously contaminate aquatic habitats in Canada. Subsequent studies have verified this prediction, as shown in the following taxa: freshwater fish (*1, 7, 8, 20, 22, 23, 32, 34*), waterfowl (*1, 5, 6, 8, 21, 33, 34, 35*), marine mammals (*9, 10, 19, 21, 22, 24, 26, 27*), and freshwater invertebrates (*12, 13, 25*).

Guidelines were established in 1970 by the Canadian Food and Drug Directorate which banned the sale of edible portions of fish containing in excess of 0.50 ppm mercury (wet weight). Therefore, in Manitoba, 356 ducks were collected during 1971 and 1972 to ascertain whether they contained elevated mercury levels (> 0.50 ppm). Some of the lakes, streams, and marshes of Manitoba may have received mercury inputs from Saskatchewan via the Saskatchewan River (*5, 36*), from Ontario via the English-Winnipeg River (*5*), and from the United States via the Red River, as well as from sources within the province.

The present study was undertaken because studies on mercury residue levels in Canadian prairie ducks (*33*) did not adequately cover Manitoba. Of 210 ducks collected, only 11 were from Manitoba and provided minimal information on potential mercury contamination of areas in Manitoba. In addition to our main concern regarding elevated mercury levels as a potential health hazard, the authors wish to document the concentration of mercury in various tissues of spring and fall migrating waterfowl and the concentration of mercury in waterfowl reared in Manitoba and to determine relationships useful in predicting concentrations of mercury in the liver and breast muscle of waterfowl.

Experimental

STUDY AREA, MATERIALS, AND METHODS

Waterfowl used in total mercury analyses were shot with 12-gauge shotgun on marshes from the Saskatchewan River Delta east of the Pas, Manitoba (Rat Hunting Creek, Summerberry River, Hill Island, Head River, Two Islands, Tom Lamb Wildlife Management Area, Little Frog Creek, and Grand Rapids) and from the Lake Winnipeg Area (Netley Marsh, Riverton, Hodgson, Hecla Island, Stead, Pine Falls, and Gypsumville). These areas were selected because of the occurrence of mercury-contaminated fish (*23*; A. J. Derksen, unpublished data) and the presence of marshes which are important to duck reproduction.

SAMPLING

To compare mercury in liver and breast muscle tissues, 136 ducks were collected. In addition to these tissues, primary feathers were obtained from 49 of the speci-

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mens for mercury analysis. The samples were distributed as follows: 42 ducks in 1971 and 50 in 1972 were collected from the Saskatchewan River Delta. Also in 1971, 44 ducks were collected from the Lake Winnipeg area. Approximately half the samples were collected during April and early May; the remainder were collected during late August in the Saskatchewan River Delta and during October and early November in the Lake Winnipeg area. An additional 220 ducks, from which only breast muscle was taken for analysis, were collected over the two-year period from both areas.

Immature refers to young of the year collected on either natal areas or areas adjacent to natal sites.

TISSUES

The breast muscle, weighing approximately 20 g, was dissected from the left side of the keel of each frozen specimen. A minimum of 10 g sample of liver tissue was removed from the left lobe. Tissue samples were wrapped in aluminum foil, stored in jars, and kept frozen until analysis. The sixth through tenth primary feathers, usually from the left wing, were stored in envelopes until analysis. Before storage, feathers were cleaned according to the method of Kelsall (*18*).

RESIDUE ANALYSIS

Breast muscle, liver, and feather samples from the two study areas were analyzed by the Environmental Management, Winnipeg. Mercury was determined by flameless atomic absorption spectrophotometry (*2*). The method was slightly modified: Only 10 mL $KMnO_4$ reagent was necessary to digest duck flesh. The method was reliable within ±10 percent of the actual value (*6*) and our spiked samples showed total recovery. All values are given as total mercury on a ppm wet weight basis.

Arithmetic means are presented throughout the text for convenience, but statistical comparison of laboratory results were made by the nonparametric Mann-Whitney U method (*28*).

Results and Discussion

RESIDUES IN BREAST MUSCLE

Low concentrations of mercury (Table 1) were found in the breast muscle of adult ducks collected during spring 1971 and 1972 from the Saskatchewan River Delta. Average value for both years was 0.10 ppm mercury for 110 dabbling ducks and 0.19 ppm for 52 diving ducks. The concentration of mercury in breast muscle of dabblers from Lake Winnipeg was comparable at 0.16 ppm ($n = 17$), while mercury concentration in divers was significantly higher [Mann-Whitney U test (*28*), $P < 0.05$] at 0.43 ppm ($n = 7$).

TABLE 1. *Mercury levels in the breast muscle of 16 species of waterfowl collected in Manitoba during 1971 and 1972*

		PPM Hg Wet Wt					
		Saskatchewan River Delta			Lake Winnipeg		
Species/ Season/Age		Number	Mean	Range	Number	Mean	Range
Mallard							
Spring	1971	12	0.17	0.05–0.45	2	0.11	0.03–0.18
	1972	19	0.12	0.02–0.42			
Fall	1971 Im	11	0.12	0.04–0.48	6	0.12	0.06–0.19
	1971 Ad	3	0.06	0.03–0.09	6	0.16	0.08–0.23
	1972 Im	10	0.19	0.07–0.30			
	1972 Ad	7	0.12	0.05–0.22			
Pintail							
Spring	1971	1	0.04		2	0.11	0.10–0.12
Fall	1971 Im	2	0.15	0.14–0.16	3	0.17	0.04–0.23
Gadwall							
Spring	1971	10	0.05	0.02–0.08	1	0.04	
Fall	1971 Im	9	0.07	0.04–0.11			
	1971 Ad	2	0.08	0.06–0.11			
	1972 Ad	1	0.13				
American wigeon							
Spring	1971	10	0.06	0.02–0.08			
	1972	1	0.04				
Fall	1971 Im				3	0.06	0.05–0.08
	1971 Ad	3	0.07	0.04–0.08	2	0.03	0.02–0.05
	1971 Ad	1	0.66				
American green winged teal							
Spring	1971	3	0.08	0.06–0.11	3	0.08	0.04–0.12
	1972	10	0.18	0.12–0.23			
Fall	1971 Im				5	0.18	0.09–0.22
	1971 Ad	2	0.30	0.06–0.54			
	1972 Im	2	0.25	0.12–0.39			
	1972 Ad	1	0.33				
Blue-winged teal							
Spring	1971	12	0.26	0.06–0.65	6	0.20	0.08–0.31
	1972	20	0.23	0.10–0.35			
Fall	1971 Im	1	0.18		3	0.53	0.44–0.62
	1971 Ad	5	0.13	0.09–0.19	3	0.49	0.12–0.76
	1972 Im	11	0.09	0.05–0.16			
	1972 Ad	2	0.16	0.13–0.19			
Shoveler							
Spring	1971	11	0.35	0.15–0.51	3	0.29	0.20–0.39
	1972	1	0.37				
Fall	1971 Im	3	0.12	0.10–0.15			
	1971 Ad	2	0.19	0.13–0.25	1	0.28	
	1972 Im	1	0.13				
	1972 Ad	1	0.74				
Redhead							
Fall	1971 Im	1	0.12		1	0.10	
	1971 Ad				1	0.04	
Canvasback							
Spring	1971	7	0.08	0.05–0.12			
Fall	1971 Im	8	0.09	0.02–0.26			
	1971 Ad				1	0.02	
	1972 Im	1	0.12				
Greater scaup							
Fall	1971 Im	2	0.20	0.12–0.27			
Lesser scaup							
Spring	1971	13	0.16	0.08–0.33	3	0.32	0.08–0.76
	1972	21	0.19	0.06–0.70			
Fall	1971 Im	5	0.19	0.11–0.39	6	0.16	0.07–0.27
	1971 Ad	2	0.16	0.10–0.22			
	1972 Im	11	0.16	0.09–0.36			
	1972 Ad	8	0.24	0.08–0.86			
Ring-necked duck							
Spring	1971	1	0.03				
	1972	3	0.08	0.07			
Fall	1971 Im				3	0.08	0.06–0.10
Common goldeneye							
Spring	1971	2	0.63	0.58–0.67			
Fall	1971 Im				1	0.72	
	1971 Ad				2	0.12	0.12–0.13
Bufflehead							
Spring	1971	5	0.36	0.10–0.79	4	0.52	0.36–0.84
Fall	1971 Ad				3	0.28	0.10–0.56
Ruddy duck							
Fall	1971 Im	1	0.08				
Hooded merganser							
Fall	1972 Ad	1	0.26				

Mercury levels in fall adult migrants differed from levels in spring migrants in the comparison of 1971 fall dabblers to 1972 spring migrant dabblers returning to the Saskatchewan River Delta. The 1972 spring dabblers averaged 0.18 ppm mercury compared to 0.13 ppm for 1971 fall dabbler adults ($P < 0.001$). This difference may reflect the uptake of mercury on the wintering grounds, the influence of dabblers originating from other areas, or a minor difference in the composition of dabbler species in 1971 and 1972.

The mercury in breast muscle of adult ducks collected in fall 1971 from Lake Winnipeg sites averaged 0.23 ppm for 2 dabblers and 0.16 ppm for 7 divers.

Mallard, pintail, lesser scaup (*Aythya affinis*) and canvasback (*A. valisineris*) (*33*) collected from western Canada in late summer or fall 1969 and 1970, when mercury was used extensively in agriculture as a seed dressing for grain and in fungicides (*5*), revealed lower levels of mercury than the values reported here (Table 1). The present values for breast muscle are comparable to those of Pearce et al. (*21*) for waterfowl collected in eastern Canada during 1971 and 1972. They reported an average of 0.15 ppm in 146 dabbling ducks and 0.13 ppm mercury in 61 diving ducks. These differences may result from the accumulation and magnification of mercury in large, stream-fed habitats compared to a lower potential for mercury concentration in small prairie potholes, and subsequent differing availability to waterfowl.

Immature dabbling ducks from the Delta collections averaged 0.13 ppm ($n = 50$) for 1971 and 1972 while Lake Winnipeg immatures averaged 0.19 ppm ($n = 20$). The immature dabblers from both the Saskatchewan River Delta and the Lake Winnipeg area in 1971 had relatively lower mercury concentrations in their breast muscles than the adults collected during the spring from these areas, although this difference was not significant. There were significant differences between the Delta immatures for 1971 and 1972 (0.15 ppm, $n = 24$, $P < 0.05$). These differences were attributed to the higher mercury load in the breast muscle of immature blue-winged teal (*Anas discors*) in the 1971 Lake Winnipeg sample and in the mallard from the 1972 Saskatchewan River collection. The 1972 immature mallards (0.19 ppm, $n = 10$) had mercury levels that were 58 percent higher than levels in the 1971 immatures (0.12 ppm, $n = 12$). The increase in mercury load in the waterfowl suggests an increase in mercury contamination within the Saskatchewan River Delta, but authors were not able to determine the contamination source.

Immature lesser scaup, common goldeneye (*Bucephala clangula*), bufflehead (*B. albeola*), ring-necked duck (*Aythya collaris*), ruddy duck (*Oxyura jamaicensis*), and canvasback had low levels of mercury in breast muscles; these levels were most similar to those in the immature dabblers. In 1971, immature Lake Winnipeg divers averaged 0.02 ppm ($n = 11$) whereas those from the Delta averaged 0.13 ppm ($n = 14$) in 1971 and 0.15 ppm ($n = 13$) in 1972. There were no significant differences between either years or areas.

Mercury residues in the breast muscle of dabblers exceeded 0.05 ppm in 10 of 239 samples, eight of which were adults. This sample included adult and immature blue-winged teal 1971 fall collections from the Delta and Lake areas, and American wigeon (*Anas americana*) and shoveler collected during fall 1972 from the Saskatchewan River Delta.

These dabblers, shovelers, and blue-winged teal as well as the American green-winged teal (*Anas crecca*) had higher mercury residue concentrations in breast muscle than did other species. The three species do not field-feed so are not directly exposed to treated gain. Thus their mercury uptake must involve aquatic food chains. Feeding studies indicate that these species depend heavily on gastropods and crustaceans (*3, 4, 29, 31*) which are known magnifiers of methyl mercury (*14*). Immatures of these species, which are primarily animal feeders, would be useful indicators of mercury contamination sites. Unfortunately the immature blue-winged teal collected during November 1971 in the Lake Winnipeg area were fledged and therefore may not represent the area of collection.

In 10 of 17 divers, mercury concentration in breast muscle exceeded 0.5 ppm. Goldeneye and bufflehead were collected from both localities during fall 1971. Contaminated lesser scaup were obtained from the Lake area in spring 1971 and from the Delta in fall 1972. Nine of the 10 diver specimens were adult. The percent contamination in divers exceeding 0.5 ppm mercury in breast muscle was higher in goldeneye and buffleheads, 60 percent (3/5) and 33 percent (4/12), respectively, compared to 4 percent (3/69) for lesser scaup.

MERCURY RESIDUES IN LIVER AND FEATHER

Mercury residues in the livers of adult dabbling ducks (Table 2) collected during spring 1971 and 1972 from the Saskatchewan River Delta averaged 0.45 ppm ($n = 12$) and 0.46 ppm ($n = 16$), respectively, whereas the Lake Winnipeg sample of spring 1971 averaged 0.61 ppm ($n = 17$). None of the differences in mercury levels in liver for ducks collected by year, area, or season were significant.

In 1971, livers of immature dabblers from the Lake Winnipeg area contained 0.45 ppm ($n = 9$) while

TABLE 2. *Mercury levels in liver tissue and feathers of 16 species of waterfowl collected in Manitoba during 1971 and 1972*

Species/Season/Age	Saskatchewan River Delta						Lake Winnipeg		
	Liver, ppm Hg			Feathers, ppm Hg			Liver, ppm Hg		
	Number	Mean	Range	Number	Mean	Range	Number	Mean	Range
Mallard									
Spring 1971	3	0.32	0.24–0.43				2	0.35	0.10–0.60
1972	5	0.27	0.17–0.42	5	1.58	1.04–2.51			
Fall 1971 Im	3	0.13	0.05–0.19				2	0.19	0.15–0.21
1971 Ad	1	0.10					1	1.03	
1972 Im	5	0.46	0.06–0.98	5	1.20	0.74–1.83			
Pintail									
Spring 1971							2	0.23	0.20–0.26
Fall 1971 Im	1	0.25					2	0.43	0.21–0.64
1971 Ad	1	0.25							
Gadwall									
Spring 1971	2	0.14	0.13–0.14				1	0.18	
Fall 1971 Im	3	0.17	0.11–0.26						
1971 Ad	1	0.20							
1972 Ad	1	0.40		1	0.80				
American wigeon									
Spring 1971	3	0.13	0.09–0.16						
1972	1	0.04		1	3.06				
Fall 1971 Im	1	0.13					2	0.09	0.05–0.13
1971 Ad	1	0.13					1	0.09	
1972 Ad	1	0.71		1	1.25				
American green-winged teal									
Spring 1971							3	0.34	0.28–0.37
1972	4	0.39	0.31–0.47	4	0.92	0.56–1.37			
Fall 1971 Im							2	0.80	0.66–0.93
1971 Ad	1	0.74							
1972 Im	2	0.31	0.48–1.13	2	2.00	0.79–4.21			
1972 Ad	1	0.66		1	7.02				
Blue-winged teal									
Spring 1971	2	0.84	0.73–0.94				6	0.75	0.25–1.20
1972	5	0.63	0.34–0.94	5	3.16	1.40–6.09			
Fall 1971 Im	1	0.45					1	1.09	
1971 Ad	2	0.43	0.19–0.67				1	1.05	
1972 Im	4	0.16	0.11–0.21	4	1.10	0.39–2.01			
Shoveler									
Spring 1971	2	1.23	0.59–1.86				3	1.18	0.95–1.30
1972	1	1.27		1	10.46				
Fall 1971 Im	1	0.38							
1971 Ad	1	0.39					1	1.02	
1972 Im	1	0.12		1	0.72				
1972 Ad	1	0.97		1	3.44				
Redhead									
Fall 1971 Im	1	0.39							
1971 Ad							1	0.11	
Canvasback									
Spring 1971	2	0.38	0.28–0.48						
Fall 1971 Im	2	0.10	0.07–0.12						
1971 Ad							1	0.06	
1972 Im	1	0.15		1	0.69				
Greater scaup									
Fall 1971 Im							1	0.36	
Lesser scaup									
Spring 1971	3	0.89	0.44–1.40				3	1.00	0.42–2.10
1972	6	0.47	0.16–0.85	6	1.69	1.00–2.98			
Fall 1971 Im	3	0.41	0.31–0.53				1	0.40	
1971 Ad	1	0.55							
1972 Im	5	0.27	0.18–0.37	5	1.25	0.57–2.66			
Ring-necked duck									
Spring 1972	3	0.12	0.05–0.17	3	1.26	0.56–2.33			
Fall 1971 Ad							1	0.58	
Common goldeneye									
Spring 1971	2	3.60	3.60						
Fall 1971 Ad							1	0.58	
Bufflehead									
Spring 1971	1	3.80					4	1.78	1.40–2.40
Fall 1971 Ad							1	0.36	
Ruddy duck									
Fall 1971 Im	1	0.25		1	0.90				
Hooded merganser									
Fall 1972 Ad	1	0.87		1	0.26				

young from the Delta area carried mercury loads of 0.22 ppm ($n = 9$) in 1971 and 0.29 ppm ($n = 12$) in 1972. Manitoba-reared divers exhibited mercury concentrations similar to most immature dabbler species sampled: Lake Winnipeg samples contained 0.45 ppm ($n = 3$) while the Saskatchewan River Delta immatures contained 0.32 ppm ($n = 6$) in 1971 and 0.25 ppm ($n = 7$) in 1972. There were no significant differences between area or within year comparisons of young. Differences did occur between amounts of mercury carried by adults and young within the study areas; in 1971 adult divers from both localities contained higher mercury loads in liver tissue than did the young. Immature dabblers reared in the Saskatchewan River Delta in 1972 had a lower liver mercury load compared to both the spring ($P < 0.05$) and fall adult dabblers ($P < 0.01$), where species composition was nearly identical.

Mercury levels in livers of dabblers collected at Maynard and Sydney Lakes in northwestern Ontario (*6*) were similar to the present results, whereas ducks collected on the more contaminated Ball and Clay Lakes exceed most of the values recorded for both Manitoba localities (Table 2). Slightly higher values of total mercury were recorded in liver of various aged shovelers (*Anas clypeata*) and pintail collected in North Dakota (*19, 30*) compared to these species collected in Manitoba. Vermeer and Armstrong (*33*) reported lower levels of mercury in livers of ducks shot in the three prairie provinces than those reported for Manitoba in the present study, except in a common merganser (*Mergus merganser*).

Feathers collected during spring 1972 at the Delta averaged 1.55 ppm mercury ($n = 9$) for divers and 2.56 ppm ($n = 16$) for dabbling ducks, whereas adult dabblers shot during fall contained 3.12 ppm ($n = 4$). Both the immature dabbling and diving ducks had lower mercury residue levels in their primary feathers than either spring or fall adults. Immature dabblers averaged 1.34 ppm ($n = 12$) and divers averaged 1.11 ppm mercury ($n = 7$). Approximately the same species composition was represented in spring and fall samples.

RELATIONSHIPS BETWEEN MERCURY RESIDUES IN FEATHERS, LIVER, AND BREAST MUSCLE

If the relationship of mercury residues in feathers, liver, or wing muscle to those in breast muscle was known and was reasonably constant, one might use the best indicator in a large-scale sampling program to guard against a potential health hazard.

Several indices have been used: feather to breast muscle, breast muscle to liver (*9, 33*), wing muscle to breast muscle (*2, 34*), and breast muscle to brain (*9*). Authors considered three relationships: feather to breast muscle, feather to liver, and breast muscle to liver. The divers and dabblers were divided by season (spring and fall) and by age (adult or immature) for the data collected from the Saskatchewan River Delta in 1972. Unfortunately, the small size of the sample did not permit comparisons of tissues at the species level.

Dabbler results indicate that feathers containing mercury are ideal for predicting mercury levels in muscle and liver of immatures and spring adults (Table 3). Small sample size and lack of data limit the extent to which data for divers may be appraised. The feather-to-liver relationship was highly significant in immature divers as was the breast-muscle-to-liver comparison of spring adult divers. Flightless young waterfowl, Class IIIa (*11*), would provide an excellent indicator for mercury pollution in natal areas since feather material as illustrated in Table 3 permits the prediction of mercury in tissue such as liver and muscle. Moderate numbers of flightless young are captured each year during banding operations in Canada and the United States (M. Smith, Fish and Wildlife Service, U.S. Department of the Interior and D. Nieman, Canadian Wildlife Service, personal communication, 1977).

Vermeer and Armstrong (*33*) found significant correlation between feather and breast muscle residues in adult pintails collected during fall but not in immatures of the species. This may be a result of the season and availability of food as well as the spatial distribution relative to sources of contamination and to collection sites.

TABLE 3. *Correlation coefficients between mercury levels (ppm) in various tissue combinations for Saskatchewan River Delta waterfowl collected in 1972*

Tissues	Dabblers			Divers		
	Spring Adults	Fall Adults	Immatures	Spring Adults	Fall Adults	Immatures
Feather to liver	0.588* (16)	0	0.665* (12)	0	N.A.[1]	0.821*** (9)
Feather to muscle	0.450* (15)	0	0.814*** (12)	0	N.A.	0
Muscle to liver	0.678** (16)	0	0.617* (12)	0.957** (9)	N.A.	0

NOTE: Sample size is given in parentheses.
$P <$ *0.05; **0.01; ***0.001.
[1] No data available.

POTENTIAL INFLUENCE OF MERCURY ON WATERFOWL POPULATIONS

A comparison of liver mercury levels in Manitoba ducks with experimental results obtained by Heinz (*15–17*) suggests that the reproduction of divers and possibly some dabbler species (*19*) may be affected by mercury contamination. Heinz (*16, 17*) observed that the reproductive success of second and third generations of mallard hens fed a diet containing 0.5 ppm mercury was lower than in the controls. The growth of their ducklings was also slower than that of the control ducklings. The average liver mercury levels in spring divers from Manitoba exceed 1.00 ppm. This mercury load, accompanied by other stresses (parasite load, pesticide residues) could create some subtle population changes. This requires further study, especially between physiologists and population biologists.

Acknowledgments

We thank Dick Robertson, Barry Jahn, Don Rusch, and Ralph Urban of the Department of Renewable Resources and Transportation Services, Manitoba, for collecting the waterfowl. Also we thank Don Rusch for his assistance during the initial stages of the study. We thank I. M. Price, and J. A. Keith, Canadian Wildlife Service, and V. Powers, University of Saskatchewan, for their constructive comments in reviewing this paper. G. E. J. Smith, Canadian Wildlife Service, Ottawa, provided statistical advice.

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Organochlorine Residues in Fish of Lake Texoma, October 1979

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ABSTRACT

Fillets from 99 fish, representing 11 species and three areas within Lake Texoma, were examined for residues of common organochlorines. Statistical analyses were conducted to determine the relationship of residues in fish fillets to trophic level and to geographical location of the sample.

Most species contained PCBs at levels up to 1100 ng/g and p,p'-DDE as high as 127 ng/g. p,p'-TDE and o,p'-DDT were not found in carnivores, but were present in herbivores and detritivores in amounts up to 36 ng p,p'-TDE/g and 17 ng o,p'-DDT/g. Heptachlor also was not found in carnivores, but was present as high as 37 ng/g in the other two classes. Chlordane ranged to 24 ng/g and was detected in all trophic levels. Dieldrin and p,p'-DDT were present in detritivores and carnivores up to 144 ng dieldrin/g and 410 ng p,p'-DDT/g. Neither substance was found in herbivores. Mirex, endrin, and heptachlor epoxide were present only at low levels. Statistically significant differences ($P = 0.05$) were found between trophic levels for seven of the eleven organochlorine compounds. No correlation ($P = 0.05$) was found between fillet concentrations of any parameter and geographical location of the sample.

Introduction

Lake Texoma is a 36,032-hectare (ha) impoundment located at river mile 726 on the Red River. Completed in January 1944 by the U.S. Army Corps of Engineers, the lake occupies portions of both Texas and Oklahoma (Fig. 1). Lake Texoma was constructed for hydropower generation and flood control, and is also used for water supply, navigation flows, sport and commercial fishing, and recreation. At normal pool level, the maximum depth is 34 meters and the mean depth is approximately 9.4 meters. The water has been described as well buffered with carbonates (pH 8.0–8.7), moderately to highly mineralized, and dominated by sodium and calcium salts of sulfates and chlorides (*5*). The lake is thermally stratified during the summer months, and due to the high chloride content of the water, also exhibits haloclines (*3*).

The Lake Texoma watershed covers 102,899 sq. km and is predominantly cropland and pasture. Principal crops grown in the basin are wheat, cotton, and grain sorghum. Except for petroleum production, there is little industry in the Texoma drainage.

This study was conducted to determine concentrations of selected organochlorine compounds, including DDT and metabolites, chlordane, heptachlor, heptachlor epoxide, dieldrin, endrin, mirex, and polychlorinated biphenyls (PCBs), in fillets from fish of Lake Texoma. In addition, we wanted to ascertain if concentrations of these substances varied with trophic level of the fish or geographical location of the sample.

Sampling and Analysis

Ninety-nine fish, representing 11 species, were collected from three areas of Lake Texoma (Fig. 1). Experimental gill nets and modified fyke traps were used on October 2 and 3, 1979, to collect all fish. No attempt was made to select for particular sizes of fish in the sample, although the sampling equipment was not well suited for taking either very large or very small individuals.

Fish species were grouped into three trophic levels as follows:

Herbivores: Gizzard shad (*Dorosoma cepedianum*)
Detritivores: Carp (*Cyprinus carpio*), channel catfish (*Ictalurus punctatus*), smallmouth buffalo (*Ictiobus bubalus*), river carpsucker (*Carpiodes carpio*)
Carnivores: Striped bass (*Morone chrysops*), white crappie (*Pomoxis annularus*), largemouth bass (*Micropterus salmoides*), blue catfish (*Ictalurus furcatus*), flathead catfish (*Pylodictus olivarus*)

Although the feeding habits of some of these species overlap, these groupings provide general trophic levels. These species were chosen not only based on their trophic level, but also because, with the exception of gizzard shad, they are prime contributors to the commercial or sport fishery.

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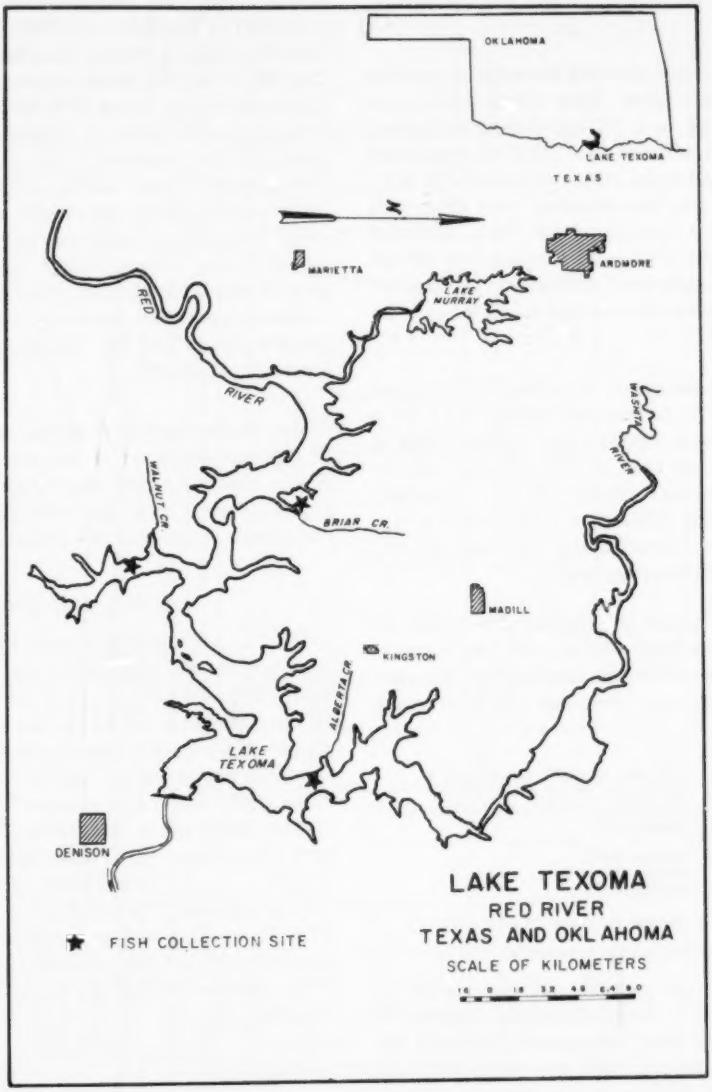

FIGURE 1. *Sampling sites on Lake Texoma, October 1979*

A fillet was removed from each fish, wrapped in aluminum foil, and transported to the laboratory where each was frozen for later analysis.

Fish fillet samples were analyzed by Texas Instruments Science Services Division under contract with the Corps of Engineers. Laboratory analysis of the fillets followed methods recommended by the Food and Drug Administration (FDA), U.S. Department of Health and Human Services (*2*). Approximately 25 g fish flesh, free of skin, bone, and organs, was weighed to four significant figures and placed in a Waring blender with an equal volume of sodium sulfate and 150 ml petroleum ether. The mixture was blended at high speed for 2 minutes. The solution was decanted through E.D. 515 fluted filter paper into a 500-ml flask. The residue was extracted with two additional 150-ml portions of petroleum ether as described above, and the extracts were filtered and combined in the 500-ml flask. The blender, filter paper, and contacts were washed with a final 10-ml portion of petroleum ether, and the total extract was transferred to a 500-ml Kuderna-Danish concentrator. The volume of the extract was reduced to 10 ml over an 80°C water bath, and the concentrated extract was quantitatively trans-

ferred to a 125-ml separatory funnel for acetonitrile partitioning.

The natural fish oils were removed from the extract by washing the petroleum ether three times with 40-ml aliquots of acetonitrile in a 125-ml separatory funnel. The acetonitrile was collected in a 1000-ml separatory funnel, and 700 ml water and 40 g sodium chloride were added. This mixture was then extracted three times with 100-ml aliquots of petroleum ether. The combined petroleum ether fractions were transferred to a 500-ml Kuderna-Danish concentrator through a column of sodium sulfate and were concentrated to 10 ml over an 80°C water bath.

This 10-ml sample concentrate was loaded on a prewashed, 10 mm × 30 cm column packed with 12 g Florisil (PR grade) and topped with 1 inch of sodium sulfate. The sample was then eluted from the column with 300 ml of 6 percent diethyl ether in petroleum ether. Each sample was reduced to a final volume of 5 ml in a Kuderna-Danish concentrator and stored at 4°C in a glass vial with a Teflon-lined cap.

The samples were originally analyzed for PCBs as Aroclor 1254, using a Perkin-Elmer 910 gas chromatograph equipped with a ^{63}Ni electron-capture detector. Instrument parameters and operating conditions were as follows:

Column:	6-ft glass, 2-mm-ID, packed with a mixture of 1.5 percent SP 2250 and 1.95 percent SP 2401 on 100–120-mesh Supelcoport
Temperatures:	injector 250°C column 200°C detector 250°C
Carrier gas:	nitrogen flowing at 30 ml/minute
Injection volume:	2 µl extract in petroleum ether

Because a number of the samples exhibited significant peaks at retention times corresponding to chlorinated pesticides, the samples were subsequently analyzed for pesticides, using a Tracor 560 gas chromatograph equipped with a ^{63}Ni electron-capture detector. Instrument parameters and operating conditions for the pesticide analyses were as follows:

Column:	10 meter, 0.25-mm-ID glass capillary coated with OV–101
Temperatures:	injector 250°C column 200°C detector 350°C
Carrier gas:	Helium flowing at 2.5 ml/minute
Make-up gas:	Nitrogen flowing at 70 ml/minute
Injection:	2 µl extract in petroleum ether plus 1 µl isooctane.

Recorder was zeroed with the column at 200°C. Column temperature was reduced to 50°C and an injection was made in the splitless mode for 30 seconds. The injection port was then purged and the column temperature was increased ballistically to 200°C.

Each sample was analyzed for *p,p'*-DDE, *p,p'*-TDE, *p,p'*-DDT, *o,p'*-DDT, *o,p'*-TDE, heptachlor, heptachlor epoxide, dieldrin, mirex, chlordane, and endrin. Detection limit for the above organochlorine pesticide residues was 1.0 ng/g, and 10.0 ng/g for Aroclor 1254. To ensure quality results, a reagent/glassware blank was generated and analyzed with each batch of 20 samples. Five percent of the samples analyzed were re-analyzed by a second person and results were within ± 15 percent. In addition, sequential recovery data and spiked recovery data were generated for 5 percent of all samples analyzed. Sequential recovery yielded 99 percent recovery from the initial extractions. Spiked recovery ranged from 95 to 104 percent. Results were not corrected for recovery.

Statistical comparison of organochlorine residues in fish of different trophic levels was conducted using Newman-Keuls multiple range test. Organochlorine residues in the fillets were correlated with geographical location of the sample by analysis of variance.

Results and Discussion

PCBs (as Aroclor 1254) were found in all species except largemouth bass, and were present in all trophic levels. Eighty-eight percent of the herbivores, 37 percent of the carnivores, and 84 percent of the detritivores contained PCBs. Median and maximum concentrations in the fillets are shown in Table 1. No significant difference ($P = 0.05$) was found between levels of PCBs in detritivores and those in herbivores. PCB levels in fillets of both herbivores and detritivores were significantly greater ($P = 0.05$) than those in carnivores. No significant correlation ($P = 0.05$) was found between levels of PCBs in fillets and geographical location of the sample. None of the fish violated either the FDA current PCB standard of 5 µg/kg or the proposed standard of 2 µg/kg (*1*).

CHLORDANE

Chlordane was present in all herbivores and detritivores except channel catfish, but was found in only two carnivorous species, striped bass and flathead catfish. It was present in 57 percent of the herbivores, 47 percent of the detritivores, and 4 percent of the carnivores. The greatest amount found was 24 ng/g in a smallmouth buffalo (Table 1). Levels of chlordane in fillets were significantly different ($P = 0.05$) in both detritivores and herbivores when compared to carnivores. There was no significant difference ($P = 0.05$) between levels in detritivores and herbivores. No significant correlation ($P = 0.05$) was indicated between chlordane levels in fillets and sample location. Zitko (*8*) deemed similar levels of chlordane in some marine species not toxicologically significant.

TABLE 1. *Concentrations (ng/g) of selected organochlorine residues in fillets of fish from Lake Texoma, October 1979*

Species	Number	PCBs		Chlordane		Dieldrin		Mirex		Endrin		*p,p'*-DDE		*p,p'*-TDE		*o,p'*-DDT		*p,p'*-DDT		Heptachlor		Heptachlor Epoxide	
		Med.	Max.	Med.	Max.	Med.	Max.	Med.	Max.	Med.	Max.	Med.	Max.	Med.	Max.	Med.	Max.	Med.	Max.	Med.	Max.	Med.	Max.
HERBIVORE																							
Gizzard shad	14	105	460	2	17	0	0	0	40	0	0	15	505	0	3	0	11	0	0	0	37	0	0
Total	14	105	460	2	17	0	0	0	40	0	0	14	505	0	3	0	11	0	0	0	37	0	0
CARNIVORES																							
Striped bass	8	50	100	0	8	0	0	0	0	0	0	4	37	0	0	0	0	0	410	0	0	0	0
White bass	14	75	110	0	0	0	144	0	0	0	0	4	12	0	0	0	0	0	0	0	0	0	34
White crappie	19	0	100	0	0	0	0	0	0	0	0	0	2	0	0	0	0	0	0	0	0	0	0
Largemouth bass	3	0	0	0	0	0	0	0	0	0	0	1	3	0	0	0	0	0	0	0	0	0	0
Blue catfish	2	50	100	0	0	0	0	0	0	0	0	12	20	0	0	0	0	0	0	0	0	0	0
Flathead catfish	1	120	120	5	5	0	0	0	0	0	0	34	34	0	0	0	0	0	0	0	0	0	0
Total	47	0	120	0	8	0	144	0	0	0	0	1	37	0	0	0	0	0	410	0	0	0	34
DETRITIVORES																							
Smallmouth buffalo	13	185	1100	5	24	0	0	0	0	0	13	29	121	0	36	0	14	0	26	0	5	0	0
River carpsucker	11	100	300	1	14	0	0	0	0	0	10	35	127	0	9	0	11	0	10	0	0	0	0
Carp	7	50	100	0	6	0	0	0	0	0	0	8	54	0	0	0	0	0	0	0	0	0	0
Channel catfish	7	50	160	0	0	0	107	0	0	0	0	10	104	0	11	0	0	0	189	0	0	0	11
Total	38	100	1100	0	24	0	107	0	0	0	13	18	127	0	36	0	14	0	189	0	0	0	11

p,p'-DDE

Members of all species and all trophic levels contained *p,p'*-DDE. Levels of this isomer in fillets were as high as 505 ng/g in a gizzard shad (Table 1). By trophic level, 93 percent of the herbivores, 84 percent of the detritivores, and 53 percent of the carnivores contained detectable amounts of *p,p'*-DDE. Levels in fillets were significantly different ($P = 0.05$) between all three groups. No significant correlation ($P = 0.05$) was noted between levels of fillets and the location of the sample.

p,p'-TDE

p,p'-TDE was found in fillets from all species of herbivores and detritivores except carp. Only one shad contained this isomer, but it was found in numerous detritivores at levels up to 36 ng/g (Table 1). It was not found in any carnivores. Detritivores contained significantly higher ($P = 0.05$) levels of *p,p'*-TDE than did either herbivores or carnivores. There was no significant difference ($P = 0.05$) between concentrations of *p,p'*-TDE in fillets of herbivores and those in carnivores. There was also no significant correlation ($P = 0.05$) between levels of *p,p'*-TDE in fillets and geographical location of the sample.

o,p'-DDT

Channel catfish and carp were the only species of detritivores which did not contain *o,p'*-DDT. However, it was found in only one individual herbivore and in no carnivores. The maximum amount found was 14 ng/g in a smallmouth buffalo (Table 1). Significantly different ($P = 0.05$) amounts of this substance were found between all three trophic levels. No significant correlation ($P = 0.05$) was found between levels of *o,p'*-DDT in fillets and sample location. Levels of *o,p'*-DDT found in the present study were similar to levels found by Klassen and Kadoum (*4*) in whole fish samples from a Kansas reservoir. Those authors also found that concentrations were higher in the low trophic levels.

p,p'-DDT

p,p'-DDT was found in all detritivores except carp. It was not found in any herbivores and was present in only one species of carnivore, striped bass. Eleven percent of the detritivores and 4 percent of the carnivores contained *p,p'*-DDT. The largest amount was found in a striped bass fillet, which contained 410 ng/g (Table 1). This high level of DDT suggests recent contamination of this striped bass (*6*). Statistically, there was no significant difference ($P = 0.05$) between *p,p'*-DDT levels in fillets and trophic status. There was also no significant correlation ($P = 0.05$) between *p,p'*-DDT levels and geographical location of the sample.

HEPTACHLOR

Amounts of heptachlor in fillets ranged up to 37 ng/g found in a shad (Table 1). In addition to shad, only smallmouth buffalo contained heptachlor in their fillets. Heptachlor levels in herbivores were significantly greater ($P = 0.05$) than those in either carnivores or detritivores. Levels in carnivores did not differ significantly ($P = 0.05$) from those in detritivores. There was no significant correlation ($P = 0.05$) between levels of heptachlor in fillets and sample location. In a study of 20 Indiana impoundments, Vanderford and Hamelink also observed only small amounts of heptachlor in fish (*7*). In that study, whole fish samples of largemouth bass, sunfish (*Lepomis* sp.), and bullhead (*Ictalurus* sp.) at most contained only trace amounts of heptachlor.

HEPTACHLOR EPOXIDE

Heptachlor epoxide was present in fillets from one carnivore (white bass) and one detritivore (channel catfish). A fillet from the white bass contained the largest amount, 34 ng/g (Table 1). There was no significant correlation ($P = 0.05$) between fillet content and either trophic level or sample location. In the previously mentioned Indiana study (*7*), only trace amounts of heptachlor epoxide were found in the various fish classes.

ENDRIN

Endrin was not detected in any herbivores or carnivores. It was present in only 5 percent of the detritivores and was limited to smallmouth buffalo and river carpsucker. Median and maximum values found in the various species are shown in Table 1. There was no significant correlation ($P = 0.05$) between endrin content of fillets and either trophic class or sample location.

MIREX

No mirex was found in either carnivores or detritivores. Fourteen percent of the herbivores contained mirex at levels up to 40 ng/g (Table 1). Levels in herbivores were significantly greater ($P = 0.05$) than those in either carnivores or detritivores. There was no significant difference ($P = 0.05$) between levels in detritivores and those in carnivores. No significant correlation ($P = 0.05$) was found between levels of mirex in fillets and geographical location of the sample.

DIELDRIN

Dieldrin was found in fillets from only one individual in each of two species. A channel catfish contained 107 ng/g and a white bass contained 144 ng/g (Table 1). Neither value approached the FDA action level of 300 ng/g. There was no significant correlation ($P = 0.05$) between fillet content and either trophic level or sample location.

Acknowledgments

The authors thank the personnel of Texas Instruments Science Services Division, for their laboratory analyses and helpful attitude. The authors also thank S. Burks, Oklahoma State University, and B. Cox, Tulsa City-County Health Department, for their review of the manuscript.

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Effects of DDE, TDE, and PCBs on Shell Thickness of Western Grebe Eggs, Bear River Migratory Bird Refuge, Utah—1973–74 [1]

Mark L. Lindvall [2] and Jessop B. Low [3]

ABSTRACT

DDE, TDE, and polychlorinated biphenyls (PCBs) as Aroclors 1260 and 1254 were detected in low concentrations in eggs of western grebes (Aechmophorus occidentalis) *from Bear River Migratory Bird Refuge, Utah. DDE was the only contaminant which was both negatively correlated with eggshell thickness and a significant variable in a multiple regression model for predicting eggshell thickness. The eggshell thickness index for western grebe decreased 2.3 percent from pre- to post-DDT-use periods. Incubation stage appeared to have no measurable correlation with eggshell thickness. The small amount of eggshell thinning seen in western grebe eggs at Bear River Migratory Bird Refuge appeared to have no detectable effect on reproduction.*

Introduction

Field studies on shell thinning in fish-eating birds are extensive. Many authors have compared shell thickness or indexes of shell thickness in fish-eating birds between pre- and post-DDT-use periods and found significant decreases (*1, 2, 4, 5, 8, 18*). Studies have also shown a negative correlation between DDE concentration and shell thickness (*1, 2, 5, 8*). Using stepwise linear regression to analyze their data on brown pelican (*Pelecanus occidentalis*) eggs, Blus et al. (*3*) concluded that, of the contaminants measured, DDE had the greatest adverse influence on shell thickness.

Breeding biology of western grebe (*Aechmophorus occidentalis*) was studied at Bear River Migratory Bird Refuge (MBR), Utah, in 1973 and 1974 (*10*). As part of that study, the relationship between pesticide and polychlorinated biphenyl (PCB) contamination and eggshell thickness and thinning was examined. Eggs collected during pre-DDT and DDT-use periods were compared to determine the change in thickness with the advent of DDT use. Multiple regression was used to test the relationship of the various contaminants to eggshell thickness.

Analytical Methods

Ninety-three eggs were collected at Bear River MBF between 1973 and 1974. Eggs were placed in egg cartons and immediately frozen. At the time of analysis, they were allowed to come to room temperature in the laboratory.

Vernier calipers were used to measure length and width (at the widest point) of the eggs to the nearest millimeter. Each egg was then cut at the waist with scissors, and its contents were removed. The inside of the shell was rinsed with water, and the shell was allowed to dry for at least two weeks before any further measurements were made. Six standardized, equally spaced measurements of shell thickness were taken at the waist of each egg, using a Starrett Model 1010 micrometer. Thickness was recorded to the nearest 0.01 mm. Shells were then weighed to the nearest 0.01 g on a torsion balance. Lengths, widths, and weights of eggs from museums were measured by the same techniques as described above. Eggs with a 7-mm or larger blow hole were not measured.

Samples were analyzed at the Denver Wildlife Research Center. Samples were prepared for analysis by the method of Peterson et al. (*14*). Analyses were performed on a Varian Aerograph Model 2740 gas chromatograph. Instrument parameters and operating conditions follow:

Detector:	tritium foil electron-capture
Column:	2-m × 2-mm ID, packed with (1) 3 percent OV-1 on 80–100-mesh Chromosorb W, AW, DMCS; (2) 5 percent QF-1 on 100–200-mesh Chromosorb W, AW, DMCS
Temperatures:	detector 215°C injection port 200°C column 190°C
Carrier gas:	nitrogen flowing at 40 ml/minute

[1] Funding for this project was supplied primarily by the Fish and Wildlife Service, U.S. Department of the Interior, through the Utah Cooperative Wildlife Research Unit. Additional funding was also provided by the Wildlife Society and the Ecology Center, Utah State University.

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Two dissimilar columns were used to confirm the presence of the contaminants. Amounts of DDE and TDE present in samples were calculated by comparing sample peak heights with peak heights of standards. To determine DDE concentration, the sample was diluted until the background PCBs were no longer visible. Amounts of Aroclors 1260 and 1254 were calculated by comparing peak areas of samples with peak areas of standards. Because of peak overlaps, quantities of both TDE and Aroclor 1254 are estimates. That is, area or peak height of underlying PCBs was estimated and then deducted from the observed height or area to obtain the actual peak height due to TDE or the actual peak area due to Aroclor 1254. The lowest quantifiable concentrations were 0.1 ppm DDE and TDE and 1 ppm Aroclors 1254 and 1260.

Results and Discussion

DDE, TDE, and PCBs corresponding to Aroclors 1260 and 1254 were found in various concentrations in western grebe eggs from Bear River MBR (Table 1). DDE was the predominant contaminant detected, averaging 6.6 ppm. TDE averaged 1.3 ppm, and both PCBs, less than 1 ppm; data are recorded on a wet weight basis, and are not corrected for recovery.

TABLE 1. *Organochlorine levels in whole western grebe eggs collected at Bear River Migratory Bird Refuge, 1973–74*[1]

Organochlorine	Basis	Residues, ppm		
		$\bar{x}$	90% CI	Range
DDE	wet	6.6	±1.6	1.0–21.4
	lipid	76.5	±17.7	20–275
TDE	wet	1.3	±0.3	0.3–4.7
	lipid	14.9	±3.1	3–52
Aroclor 1260	wet	<1	—	<1–5.4
Aroclor 1254	wet	<1	—	<1–3.8

[1] $N = 40$.

Ratcliffe (*16*) devised an index to eggshell thickness rather than a directly measured thickness, and that index has gained wide acceptance because it is useful in measuring museum specimens in which a direct thickness measurement cannot be obtained.

Ratcliffe's index is a good estimator of shell thickness in western grebe eggs. The thickness index and average thickness of 93 eggs collected at Bear River Migratory Bird Refuge were highly correlated ($r^2 = 0.7$).

The average eggshell thickness index of the eggs collected at Bear River MBR during 1973 and 1974 was significantly smaller than the same figure for 389 pre-1940 eggs measured in museums ($F = 25.6$, $P < 0.1$). The average thickness index and standard deviation for 93 Bear River MBR eggs was 1.898 ± 0.015 mm and for 389 pre-1940 museum eggs, 1.989 ± 0.008. This is a decrease of 2.3 percent, a small but significant decrease, from pre-1940 to present. Pre-1940 eggs were used in the comparison because they represent a sample obtained before the widespread use of DDT. No difference was seen between pre-1940 eggs collected in California and Utah, and thus the two groups were pooled for the comparison.

The average eggshell thickness (direct measurement) and standard deviation of 93 eggs collected in 1973 and 1974 at Bear River is 0.38 ± 0.03 mm. Rudd and Herman (*18*) give 0.33 mm as the average eggshell thickness of eggs collected at Clear Lake, California, after TDE application to the lake. Eggs at Clear Lake had higher levels of contaminants than those collected during the present study at Bear River MBR. Rudd and Herman (*18*) also took direct measurements from pre-1940 eggs and found an average thickness of 0.389 mm, a thickness 3.1 percent greater than the present Bear River Migratory Bird Refuge collections.

The small amount of eggshell thinning seen in western grebe eggshells at Bear River MBR appeared to have little or no effect on reproduction, because no crushed, cracked, or broken eggs were seen during this study. Average brood sizes of 1.6 in 1973 and 1.8 in 1974 from Bear River compare well with the Rudd and Herman determination of a normally reproducing population (*18*).

Multiple regression with stepwise deletion was used to test the relationship of the various contaminants to eggshell thickness and eggshell thicknes index as was done by Blus et al. (*3*).

The original model for the western grebes, with all contaminants included, explained 45 percent of the variability in eggshell thickness index and 51 percent of the variability in eggshell thickness. In this model the contribution of DDE was significant at the $\alpha = 0.05$ level, and the contribution of Aroclor 1260 was significant at the $\alpha = 0.1$ level. The deletion of Aroclor 1254 and TDE from the model did not lessen the predictive power.

The model containing Aroclor 1260 and DDE explained 50 percent of the variability in eggshell thickness and 45 percent of the variability in thickness index. The contribution of DDE in this model was significant at $\alpha = 0.01$ and the contribution of Aroclor 1260 was significant at $\alpha = 0.025$. This model proved to be the best predictor of both eggshell thickness and thickness index. Deleting Aroclor 1260 from the model and forming a model with only DDE resulted in a loss of predictive power. A model with only DDE explained 37 percent of the variability in eggshell thickness and 33 percent of the variability in thickness index. The contribution of DDE was significant at $\alpha = 0.01$. Table 2 summarizes the various models discussed.

TABLE 2. *Multiple regression models for predicting eggshell thickness and thickness indexes in western grebe eggs, using organochlorine concentrations*

Model	Variable [1]	*F* Ratio	r^2 for Model
$Y_1 = 2.15 + 0.10X_1 + 0.01X_2$	1*	3.1	0.45
$- 16X_3 - 0.04X_4$	2	<0.1	
	3**	5.7	
	4	0.3	
$Y_1 = 2.18 = 0.11X_1 - 0.18X_2$	1**	7.3	0.45
	3***	29.0	
$Y_1 = 2.10 - 0.13X_2$	3***	18.9	0.33
$Y_2 = 42.89 = 1.82X_1 = 0.45X_2$	1*	3.8	0.51
$- 3.12X_3 - 0.83X_4$	2	0.2	
	3***	8.4	
	4	0.5	
$Y_2 = 43.45 = 2.19X_1 - 3.58X_2$	1***	9.4	0.50
	3***	35.6	
$Y_2 = 42.02 - 2.62X_2$	3***	21.4	0.37

NOTE: Y_1 = predicted value of eggshell thickness index; Y_2 = predicted value of eggshell thickness; X_1 = log of Aroclor 1260 concentration, values <1.0 ppm counted as log 0.5; X_2 = log of Aroclor 1254 concentration, values < 1.0 ppm counted as log 0.5; X_3 = log of DDE concentration; X_4 = log of TDE concentration.
[1] Significant at *0.1, **0.05, ***0.01.

The best multiple regression model for predicting both eggshell thickness and eggshell thickness index is the one which includes DDE and Aroclor 1260. Interpretation of this model can be aided by examination of the correlation coefficients (r values) which are given in Table 3. TDE is significantly negatively correlated with both eggshell parameters. Multiple regression analysis suggests, however, that TDE relationship to eggshell thickness and index is spurious, that it is a result of its correlation with DDE. Correlations between both PCBs and eggshell thickness and thickness index were not significant. The contribution of Aroclor 1260 to a multiple regression model was, however, significant. Interpretation of the multiple regression relationship between Aroclor 1260 and eggshell thickness or thickness index is difficult because of this lack of correlation between Aroclor 1260 and either eggshell parameter. One multiple regression model was also tested in which the log of the sum of the PCB isomers was used. This model differed little from the model in which authors considered the PCBs separately. No conclusion on the effect of Aroclor 1260 on eggshell thickness can be drawn from this analysis. The fact that Aroclor 1260 can explain variability in eggshell thickness and thickness index does, however, suggest that there is a possible interaction between Aroclor 1260 and DDE.

DDE was the only contaminant which was both correlated with and could explain variability in eggshell thickness and eggshell thickness index. Experimental studies have shown that DDE in diet can cause decrease in eggshell thickness (*6, 11, 12, 15, 20*). Experimental studies in which birds were subjected to PCBs have not shown reductions in eggshell thickness (*7, 13, 19*). These experimental results support the finding that DDE can be directly correlated to eggshell thinning in the western grebe, but that Aroclors 1260 and 1254 can not. Present analyses do, however, suggest an interaction between Aroclor 1260 and DDE.

TABLE 3. *Correlation coefficients* (r) *comparing organochlorine concentrations and eggshell parameters for western grebe at Bear River Migratory Bird Refuge, 1973–74*

Parameter	DDE	TDE	Aroclor 1254	Aroclor 1260
Thickness	−0.60*	−0.58*	−0.25	−0.01
Thickness index	−0.58*	−0.56*	−0.27	−0.03

NOTE: * Indicates significance at $\alpha = 0.01$.

Incubation stage appears to have no measurable effect on eggshell thickness or index in western grebe. Eggs were divided into four classes according to embryo development, and analysis of variance was used to test for differences between the incubation stages. Groups 1, 2, 3, and 4 contained 50, 19, 8, and 19 eggs, respectively. Significant differences were not detected between groups in either eggshell thickness or index. Declines in eggshell thickness as incubation progressed were reported by Rothstein (*17*) for cedar waxwing (*Bombycella cedrorum*) and by Kreitzer (*9*) for Coturnix quail (*Coturnix coturnix*).

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APPENDIX

Chemical Names of Compounds Discussed in This Issue

AROCLOR 1254	PCB, approximately 54% chlorine
AROCLOR 1260	PCB, approximately 60% chlorine
CHLORDANE	Technical: 60% octachloro-4,7-methanotetrahydroindane and 40% related compounds
DDE	Dichlorodiphenyldichloroethylene (degradation product of DDT)
DDT	Dichloro diphenyl trichloroethane. Principal isomer present (*p,p'*-DDT; not less than 70%): 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane
DIELDRIN	Hexachloroepoxyoctahydro-*endo,exo*-dimethanonaphthalene 85% and related compounds 15%
ENDRIN	Hexachloroepoxyoctahydro-*endo,endo*-dimethanonaphthalene
HCB	Hexachlorobenzene
HEPTACHLOR	Heptachlorotetrahydro-4,7-methanoindene
HEPTACHLOR EPOXIDE	1,4,5,6,7,8,8-Heptachloro-2,3-*epoxy*-3a,4,7,7a-tetrahydro-4,7-methanoindan
MIREX	Dodecachlorooctahydro-1,3,4-metheno-1*H*-cyclobuta[cd]pentalene
NONACHLOR	1,2,3,4,5,6,7,8,8-Nonachlor-3a,4,7,7a-tetrahydro-4,7-methanoindan
OXYCHLORDANE	1-*exo*-2-*endo*-4,5,6,7,8,8a-Octachloro-2,3-*exo*-*epoxy*-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene
PCBs (Polychlorinated Biphenyls)	Mixtures of chlorinated biphenyl compounds having various percentages of chlorine
TDE	Dichloro diphenyl dichloroethane (1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane, principal component)
TOXAPHENE	Technical chlorinated camphene (67–69% chlorine)

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U.S. Environmental Protection Agency
Washington, D.C. 20460

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